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/ **Chemistry.** — ERNST COHEN and W. D. J. VAN DOBBENBURGH: *"The influence of minute traces of Water on Equilibria of Solution"*. I.

(Communicated at the meeting of June 27, 1925)

Introductory.

In the course of our investigations on the metastability of matter made in co-operation with Messrs MOESVELD, HELDERMAN, BRUINS and KOOY [1]), our attention has been drawn to salicylic acid, as, from more than one point of view, it is of importance to get better acquainted with the relations of stability between the modifications in which this substance can appear.

During this investigation, to which we hope to return later on, we have become acquainted with phenomena so very remarkable, and, as we found out, unknown up to the present, that we have suspended our intended investigation for the moment, in order to study these new phenomena quantitatively. This paper contains a description of the results obtained up to this time.

For the sake of lucidity we do not dwell on the relation between the investigation treated in this paper, and of the metastability of matter which has led to the measurements which are to be described. For us the thing was to determine the solubility in benzene of salicylic acid which had been recrystallized from different solvents. All the solubility determinations have been carried out at 30°.50 C.

A. *The Materials used.*

§ 1. *a. Salicylic acid.* The material with which we started our work was obtained from different factories. When it was found that the different preparations gave identical results, we have, in most cases, used a preparation of KAHLBAUM at Berlin („für kalorimetrische Bestimmungen"), and after recrystallizing it from the solvents which will be mentioned later on, taken it for our investigation.

b. Benzene. A preparation which had been supplied as not containing thiophene, really answered this requirement. For some days it was left in contact with an ample quantity of phosphorous pentoxide, and then slowly distilled [1]) by means of an electric lamp which was used as heater. The flask in which the distillate was collected, was protected from moisture by a tube, filled with $CaCl_2$. It was closed afterwards with a glass stopper. The stock of benzene obtained in this way was in contact with the air only when the liquid was poured out of the flask.

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[1]) Zeitschr. f. physik. Chemie **94**, 450, 465, 471 (1920); **108**, 81, 97, 100, 109 (1924); **113**, 145 (1924); **115**, 151 (1925).

c. *Ether.* This substance was treated like the benzene. The flask in which it was kept was closed with a cork.

d. *Water.* This liquid was slowly distilled out of a heavily tinned apparatus.

B. *The Preparations of Salicylic Acid.*

§ 2. The two preparations, mentioned under *A. a.* in § 1, were crystallized either from water, or from dried ether, in the way as is described hereafter, and then dried as indicated in every different case.

1. *Preparations recrystallized from water.*

a. To a certain quantity of solid salicylic acid so much water is added, that at about 100° all is dissolved, then it is filtered through a hot water funnel. By heating the filtered solution the acid is again completely dissolved. Then the flask which contains the solution, is quickly cooled in water of room temperature. The crystallized acid is sucked off on a hard filter, first dried in air between filter paper, and then dried in vacuo over P_2O_5 (for 48—72 hours).

b. The same method, as is described under *a.* is followed, but the crystallization is allowed to be very gradual.

c. Again the same method as under *a.* is applied, but the crystallization is very rapid, by pouring the solution on ice ("chilled").

When the preparations had been kept in vacuo over P_2O_5 for 48—72 hours they were sufficiently dry. This was controlled by investigating the change of weight of a few grammes of the preparation, dried in this way, after keeping it in the dessicator in vacuo for a longer period. In this way it was seen that drying for 24 hours longer did not lead to any perceptible change of weight.

2. *Preparations recrystallized from ether.*

A solution of salicylic acid in dry ether, saturated at room temperature, was put into a conical filtering flask, the tube of which is connected with a water- jet vacuum pump. The neck of the flask is closed with a rubber stopper, through which passed a rather wide glass tube. The latter is connected with three washing bottles, filled with strong sulphuric acid, care being taken that specks of the acid cannot enter the filtering flask by interposing an empty absorption bulb. When the water- jet vacuum pump is set going a (rapid) current of dry air passes through the solution. In this way some 50 grammes of dry acid can be obtained in a few hours. This preparation was likewise kept in vacuo in a dessicator over P_2O_5.

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[1]) SIDGWICK, Journ. chem. Soc. London **117**, (2) 1340 (1920).

TH. W. RICHARDS, E. K. CARVER and W. C. SCHUMB, Journ. Am. Chem. Soc. **41**, 2019 (1919).

C. The Solubility determinations.

Experimental.

1. *General Remarks.*

§ 3. The salicylic acid was shaken with the benzene in flasks *A*, as is shown in fig. 1 (capacity about 50 c.c.) When the solid and the solvent had been put in by means of a funnel with a wide stem, the flasks were sealed, and then placed into the acatene shaking apparatus, previously described by ERNST COHEN and H. R. BRUINS [1]). In our thermostat, in which this apparatus was placed, was always a BECKMANN thermometer, graduated in 0.01°. The thermometers used were compared with an instrument graduated in 0.1°, which had been calibrated by the Physikalisch Technische Reichsanstalt at Charlottenburg, and of which we had controlled the zero point. The temperature regulation was done by means of an OSTWALD regulator (capacity of the reservoir about 500 c.c.) which we filled with tetrachlorethane [2]).

The temperature fluctuations of the thermostat were, during short periods, never greater than one or two hundredths of a degree.

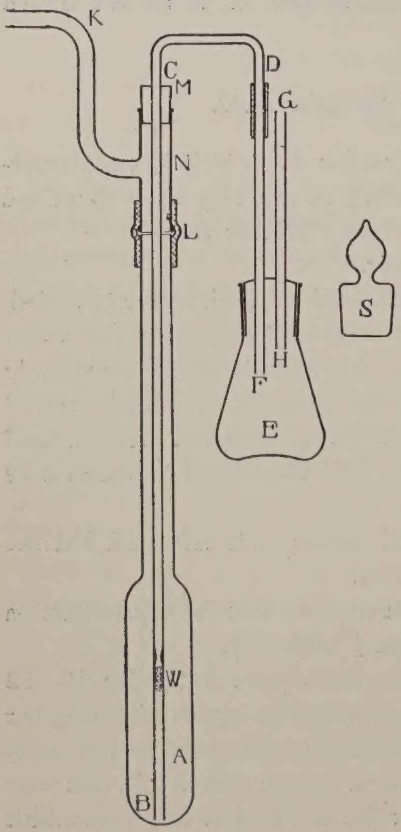

Fig. 1.

§ 4. The tapping of the saturated solutions was done by means of the apparatus shown in Fig. 1. When the shaking apparatus had been stopped, the solid was allowed to settle, the top part of the long neck of flask *A* was cut off, and the tube *B C D*, previously heated and containing a piece of cotton wool *W* at its lower end, was placed into it as quickly as possible. By means of a rubber bulb the filtered, clear, saturated solution is pressed into the flask *E*, which is immediately closed with a carefully ground glass stopper *S*. The flask is placed for a moment in cold water, in order to lessen the vapour tension over the solution, then it is completely dried and the flask with its contents is weighed.

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[1]) Zeitschr. f. physik. Chemie **93**, 43 (1918).

[2]) Zeitschr. f. physik. Chemie **117**, 143 (1925), § 6.

Of every saturated solution two samples were tapped out of the same flask; for every sample we used a separate tapping tube (*B C D* in Fig 1) which had been previously heated to the temperature of the experiment.

All the weighings (up to $^1/_{10}$ milligram) were carried out on a BUNGE balance. The weights were calibrated according to the well known method of F. KOHLRAUSCH.

2. *Analysis of the saturated solutions.*

§ 5. The technical part of the determinations was as follows: After weighing the saturated solutions in the flask *E*, which is closed with the stopper *S*, (which had been weighed beforehand) the benzene is removed by passing a dry current of air over it.

For this purpose we place the glass stopper with the tubes *G* and *F* on the flask, connect the tube *G* with the water- jet vacuum pump, the tube *F* with a battery of absorption bulbs, filled with strong sulphuric acid, interposing an empty flask, in which, eventually, specks of the acid can collect, and set the pump to work. In this way it is possible to remove 15 grams of benzene in about 6 hours.

§ 6. Different experiments have proved that this method gives accurate results, viz. that salicylic acid is not volatile in benzene vapour at temperatures below 25°. If, in the way we described, the benzene is evaporated from solutions of a concentration as we have in our actual series of experiments, we find back the quantity of salicylic acid which had been weighed into the flask, as is seen from the following determinations:

a. Weighed into the flask 0.4140 gms. of acid with about 15 gms. of benzene.
Found 0.4140 gms. of acid.

b. Weighed into the flask 0.3380 gms. of acid with about 15 gms. of benzene.
Found 0.3383 gms. of acid.

It may be pointed out here that in these determinations as well as in the later definite ones, the flasks *E*, after the removal of the benzene, were, for further control, kept for one night in the desiccator in vacuo, over phosphorous pentoxide, beside a dish filled with dry salicylic acid, so as to keep the desiccator filled with saturated vapour of this acid [1]). Change of weight could not be ascertained.

§ 7. In order to form an opinion about the possibility of reproducing the solution equilibria, and about the accuracy of the analyses, we set to work as follows: We put two parts of the same preparation of salicylic acid into two separate quantities of the same preparation of benzene, shook both flasks for the same period at the same temperature, and analysed the saturated solutions thus obtained, every solution in two separate parts *a*, *b*, respectively *c* and *d*.

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[1] See also A. L. TH. MOESVELD, Dissertation, Utrecht 1918 page 27.

In this way we found :

Solution 1: *a.* 1.04
b. 1.04
Solution 2: *c.* 1.04
d. 1.04
gms. of salicylic acid in 100 gms. of the saturated solution.

D. Final Determinations.

§ 8. All our solubility determinations have been inserted in Table 1. Some measurements which were made simultaneously for another purpose, have not been included. This is the reason why a few numbers in the first column are wanting. (See table next page.)

For further explanation of the Table we wish to observe :

The previous treatment of the solution saturated at 30°.50 C. is called *normal,* when solution equilibrium is reached from a lower temperature.

The asterisks, placed behind the solubility figures in the last column, indicate that of the solutions in question two separate flasks have been shaken. In all other cases the figures refer to two separately tapped samples of the same saturated solution.

§ 9. On closer consideration of the table we observe :

A. When the acid is crystallized from ether it never reaches a solubility in benzene greater than 1.11, neither with the normal previous treatment of the saturated solution, nor after reaching equilibrium from a high temperature. Under these circumstances we find values lying between 1.03 and 1.11. The highest figures (1.10 and 1.11) are found when equilibrium is reached from a higher temperature.

B. Preparations, crystallized from water, give, for the solubility in benzene, values lying between 1.04 and 1.38, the highest figures appearing when the solutions in contact with solute have been heated to a higher temperature. Preparations, rapidly crystallized from water, give, in general, higher values than those which have slowly crystallized from water.

C. If the acid is first crystallized from ether, and then from water, the solubility rises very markedly, (f.i. from 1.05 in experiment 3, to 1.35 in experiment 4). If, on the other hand, we crystallize first from water, and then from ether, there is a marked decrease in the solubility, (f.i. from 1.38 in experiment 31, to 1.06 in experiment 32).

§ 10. In experiment 32 we wish to call attention to the following : When experiment 31 had been made, we removed as much as possible of the saturated solution, by withdrawing it in a pipette from the shaking flask. This is laid in a horizontal position, the tube *B C D* is inserted, *K* is connected with the water- jet vacuum pump, *D* with a battery of absorption bulbs containing sulphuric acid, and dry air is sucked over the solute, until the benzene is totally removed. Then the solute is completely dissolved in dry ether which is then removed in the same way as the benzene. Then the solubility in benzene of this preparation is determined.

TABLE 1. Temperature 30°.50 C.

No. of the Experiment	Preparation crystallized from;	Previous treatment of the saturated solution at 30°.50 C.	Period of shaking in hours	Solubility gms. of solute in 100 gms. of saturated solution
3	ether	normal	20	1.03* 1.06*
4	ether, then from water	normal	23	1.36* 1.34*
9	water	first shaken for 3 hours at 48°, then at 30°.50	3	1.18 1.18
10	water	first shaken for 3 hours at 48°, then at 30°.50	24	1.22 1.23
11	ether	normal	3	1.08 1.08
12	ether	normal	21	1.09 1.09
13	water	first shaken for 3 hours at 65°, then at 30°.50	3	1.33 1.33
14	water	first shaken for 3 hours at 65°, then at 30°.50	21	1.31 1.31
15	ether	first shaken for 3 hours at 65°, then at 30°.50	3	1.10 1.10
16	ether	first shaken for 3 hours at 65°, then at 30°.50	73	1.11
17	ether	normal	286	1.09 1.06
18	ether	normal	290	1.08 1.07
19	water	normal	264	1.11 1.12

TABLE 1. Temperature 30° 50 C. *(Continued).*

No. of the Experiment	Preparation crystallized from:	Previous treatment of the saturated solution at 30°.50 C.	Period of shaking in hours	Solubility gms. of solute in 100 gms. of saturated solution
22	water slowly	normal	3	1.04 1.04 1.04 1.04
23	water slowly	normal	48	1.05 1.06 1.06 1.06
24	water chilled on ice	normal	$3^1/_2$	1.12 1.13
25	water slowly	normal	4	1.06 1.06
27	water slowly	normal	12	1.07 1.08
28	water chilled on ice	normal	3	1.14 1.14
29	water chilled on ice	normal	6	1.10 1.09
30	water chilled on ice	first shaken for 3 hours at 70°, *without* solute, then at 30°.50 C.	3	1.13 1.13
31	water chilled on ice	first shaken for 3 hours at 70°, *with* solute, then at 30°.50 C.	3	1.38 1.38
32	Solute from experiment 31, after recrystallizing from ether in the shaking-flask	first shaken for 3 hours at 70°, *with* solute, then at 30°.50 C.	3	1.06 1.06
34	first from ether, then slowly from water	normal	3	1.07 1.07

TABLE 1. Temperature 30°.50 C. *(Continued)*.

No. of the Experiment	Preparation crystallized from:	Previous treatment of the saturated solution at 30°.50 C.	Period of shaking in hours	Solubility gms. of solute in 100 gms. of saturated solution
38	water chilled on ice	first shaken for 3 hours at 70°, *with* solute, then at 30° 50 C.	3	1.24 1.24
39	first from ether, then slowly from water	first shaken for 3 hours at 70°, *with* solute. then at 30°.50 C.	3	1.23 1.23

In this way we found the figure 1.06, whereas this had first been 1.38.

§ 11. An accidental circumstance gave us at last the key to these very remarkable results.

One day we had dissolved a greater quantity of acid in boiling water, and then had poured it on ice, in order to chill the preparation suddenly. After filtration, to remove the mother liquor, we placed the acid in vacuo over phosphorous pentoxide. Though it was not quite dry the next day, we made a solubility determination with part of this preparation.

In this determination equilibrium was reached in the normal way; we found the figures 1.37 and 1.38.

When the preparation had been in vacuo over $P_2 O_5$ for 24 hours more, we found for the solubility in benzene the values 1.12 and 1.12.

§ 12. As these experiments point to the possibility, that minute traces of water had great influence on the solubility of salicylic acid in benzene, our investigation was carried on in this direction, and, as will be seen from what follows, with good results.

Our method was as follows: A preparation, crystallized from dry ether, was powdered very fine in an agate mortar, and kept in vacuo over $P_2 O_5$.

Two shaking-flasks, carefully dried were closed with glass stoppers, their weight was determined, and a certain quantity of the acid (about 1 gm.) was very carefully weighed in them. In one of the flasks water is put by means of a capillary pipette, it is again weighed, and then dry benzene (about 45 gms.) is poured into the two flasks, after which they are weighed with their contents; then they are sealed. Every time two similar flasks (one without, the other with water) were shaken simultaneously, and for the same length of time (5 to 6 hours) at 30°.50 C. Then the contents of both were analyzed in the way described above.

In the solubility figures thus found, we notice the influence of the quantities of water added, while a (very small) amount of moisture (if present) of the identical materials used was not taken into consideration.

§ 13. In this way we obtained the results, summarized in Table 2, in which the solubility is again expressed in parts of salicylic acid per 100 gms. of the saturated solution.

TABLE 2. Temperature 30°.50 C.

Solubility in wet Benzene				Solubility in dry Benzene		
No. of the Experiment	Thousandths of perc. by weight of water in the benz.	Analysis 1	Analysis 2	No. of the Experiment	Analysis 1	Analysis 2
40	4	1.01^5	1.01^5	40	1.00^3	1.00^9
41	14.7	1.04^9	1.05^0	41	1.00^3	1.00^1
42	37.4	1.09^4	1.09^7	42	1.00^7	—
43	68.2	1.18^8	1.19^3	43	1.01^3	1.01^4
44	104.2	1.30^8	1.31^0	44	1.01^5	1.01^1
45	147.8	1.34^7	1.34^9	45	1.01^1	1.01^4
46	217.1	1.35^3	1.34^9	46	1.01^1	1.02^0
47	313	1.35^1	1.35^2	47	1.02^1	1.02^0
48	excess	1.35^4	1.35^8			

§ 14. Before going deeper into the results, given in Table 1, by the light of the results summarized in Table 2, we wish to call attention to the fact that the literature contains a few data concerning the solubility of water in benzene [1]). The data given by TH. W. RICHARDS, CARVER, and SCHUMB, seem the most reliable; they found at 5°.5 C., for the solubility 0.036 per cent by weight (gms. of water in 100 gms. of the saturated solution) ; SIDGWICK gives the same figure, and GROSCHUFF found 0.03 % at 3°, and 1.14 % at 40° C. The solubility of water in benzene in the presence of salicylic acid is unknown [2]).

§ 15. If we consider the results summarized in Table 1 by the light of the data in Table 2 we shall see that the phenomena, described in Table 1, can easily be explained, if we first direct our attention to what follows.

Whereas the method of treatment of the benzene used (previous treatment and distillation with $P_2 O_5$) gives us a practically dry product [3]), from solutions of salicylic acid we obtain a preparation which always occludes minute quantities of the solvent used, as is generally the case when crystals are formed from solutions[1]). The occluded water, present in the crystals which have been formed by crystallization from water, cannot be removed from the crystals in vacuo over $P_2 O_5$; sometimes after a very long period when the crystals are powdered. Melting or subliming is necessary if we wish to reach this result quickly.

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[1]) HERZ, Ber. d. d. chem. Ges. **31**, 2669 (1898); HANTZSCH and SEBALDT, Zeitschr. f. physik. Chemie **30**, 278 (1899); TH. W. RICHARDS, CARVER en SCHUMB, Americ. Chem. Soc. **41**, 2019 (1919); SIDGWICK, Journ. chem. Soc. London **117**, 1340 (1920); GROSCHUFF, Zeitschr. f. Elektrochemie **17**, 341 (1911).

[2]) Comp. NERNST, Zeitschr. f. physik. Chemie **8**, 110 (1891), especially pag. 116.

[3]) See note 1 pag. 703.

Further it is to be borne in mind, that in crystallizing from ether, the crystals formed easily get moist, in connection with the consequent cooling, and that therefore it is possible, that traces of occluded water are formed during crystallization.

§ 16. In general, the solubility figure, found by us, will be governed by the quantity of water which, originally present in the occlusions, passes from these into the benzene, when a certain amount of solid acid dissolves into the benzene. In the preparations crystallized from ether, we might think the presence of this liquid possible, on account of the method of drying, and that traces of ether, passing into the benzene, increase the solubility of the acid in the medium thus formed. As, however, traces of ether can be easily recognized by the smell, and as we have never noticed this smell, we have as yet no reason to believe in the influence of ether. However we intend to study this point at some future time.

§ 17. Ad. § 9A. The values between 1.03 and 1.11 for preparations, crystallized from ether, are explained by the presence of water in the vacuoles, which dissolves when the solid acid dissolves in the benzene. If the solid acid with the benzene is raised beforehand to a higher temperature, a greater quantity of occluded water is dissolved in the benzene, and consequently a higher figure will be found for the solubility of the acid.

§ 18. Ad. § 9B. It is obvious that a greater amount of occluded water can be present in the preparations which are crystallized from water, than in those which have been formed from etherial solutions, and correspondingly a higher solubility figure is obtained. If solute crystallized from water is dissolved at a higher temperature, the benzene gets more watery than in the preparations formed from ether, and the solubility will consequently be higher. If so much occluded water has got into the benzene that the latter (at the temperature of the experiment, 30°.50 C.) is saturated with water, the solubility will not rise with a greater quantity of occluded water; a constant final figure is found (1.36) as the experiments actually prove.

§ 19. Ad. § 9C. The results mentioned here will be easily understood after our exposition given above.

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[1]) TH. W. RICHARDS, Zeitschr. f. physik. Chemie **46**, 189 (1903); Also Proc. Americ. Philos. Soc. **42**, 28 (1903); Also: Experimentelle Untersuchungen über Atomgewichte, Hamburg und Leipzig, 1909, Pag. 659.

§ 20. That the solubility rises with the increase of the water percentage of the benzene is in agreement with the figures which refer to dry benzene in Table 2. During the period in which the experiments 40 to 47 were made, the flask, containing the dry benzene, was opened frequently for a moment, in order to take out some of the liquid, so that water from the atmosphere could be absorbed. Indeed, the figures of the solubility indicate a slight increase.

§ 21. In the literature we have found only one accurate investigation on the solubility of salicylic acid in benzene (at a series of temperatures) viz. of WALKER and WOOD [1]). As i.a. they have also carried out some experiments at 30°.5 C., we have chosen this temperature for our determinations, so as to have a point of comparison. As WALKER and WOOD do not give further particulars about purification and drying of their preparations, we mention only that they find for the solubility 0.981 gms. of salicylic acid in 100 gms. of the saturated solution, whereas our lowest value is 1.00. Since, for want of data, we cannot form a notion of the accuracy which they attained, we shall not enter into a further discussion of their results.

§ 22. We shall postpone a discussion of several points to a later time, and mention only that the matter treated above suggests a method to determine accurately the quantity of liquid (sometimes very small) in the vacuoles of crystals [2]). We shall return to this subject at some future period.

SUMMARY.

It was demonstrated that very minute traces of water markedly increase the solubility of salicylic acid in benzene. Herein lies a method for the accurate determination of the quantity of liquid contained in the vacuoles of crystallized substances.

Utrecht, June 1925. VAN 'T HOFF-*Laboratory*.

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[1]) Journ. chem. Soc. London **73**, 618 (1898).

[2]) See also ERNST COHEN and H. R. BRUINS, Zeitschr. f. physik. Chem. **94**, 443 (1920)

Mathematics. — *"On the generalisation of the series of* VACCA". By Prof. J. C. KLUYVER.

(Communicated at the meeting of September 26, 1925.)

1. Some time ago Prof. G. VACCA simplified the proof of his remarkable expansion of EULER's constant C in a series of rational terms [1]). His method however does not allow to arrive at my somewhat generalised expansion [2]), a simple proof of which may be conducted as follows.

Putting

$$C(n) = \sum_{1}^{n} \frac{1}{k} - \log n,$$

it is easily proved that $C(n)$ decreases and that on the contrary $C(n) - \frac{1}{n}$ increases, as n tends to infinity. Therefore, a and m being integers, we infer that

$$0 < \left\{ C(am) - \frac{1}{am} \right\} - \left\{ C(m) - \frac{1}{m} \right\} < \frac{a-1}{am}.$$

Now we have by definition

$$\left\{ C(am) - \frac{1}{am} \right\} - \left\{ C(m) - \frac{1}{m} \right\} = \sum_{1}^{am-1} \frac{1}{k} - a \sum_{1}^{m-1} \frac{1}{ak} - \log a,$$

hence, denoting by β_k either $a-1$ or -1 according as k is, or is not a multiple of a, we get

$$\left\{ C(am) - \frac{1}{am} \right\} - \left\{ C(m) - \frac{1}{m} \right\} = - \sum_{1}^{am-1} \frac{\beta_k}{k} - \log a,$$

and, as we have for $m \rightarrow \infty$

$$0 = - \sum_{1}^{\infty} \frac{\beta_k}{k} - \log a,$$

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[1]) G. VACCA. Sulla costante di Eulero. Rendiconti d. R. Accad. Nat. d. Lincei. Vol. 1, serie 6a, p. 206, 1925.

[2]) These Proceedings **27**, p. 314.
Quarterly Journal. Vol. L, p. 185, 1924.

it follows that

$$0<\left\{C(am)-\frac{1}{am}\right\}-\left\{C(m)-\frac{1}{m}\right\}=\sum_{am}^{\infty}\frac{\beta_k}{k}<\frac{a-1}{am}.$$

In this equation m is changed successively into $am, a^2m, a^3m, \ldots a^{q-1}m$, and we obtain by adding the q equations

$$\left\{C(a^q\,m)-\frac{1}{a^q\,m}\right\}-\left\{C(m)-\frac{1}{m}\right\}=\sum_{h=1}^{h=q}\sum_{a^h\,m}^{\infty}\frac{\beta_k}{k}.$$

Evidently at the righthandside a definite term $\frac{\beta_k}{k}$ occurs as many times as the sequence $am, a^2m, a^3m, \ldots . a^qm$ contains a term less than k. Therefore, if x is an integer satisfying the inequalities

$$a^q\,m<n\,a<x<(n+1)\,a<a^{q+1}\,m,$$

we may write

$$\left\{C(a^q\,m)-\frac{1}{a^q\,m}\right\}-\left\{C(m)-\frac{1}{m}\right\}=\sum_{am}^{x-1}\frac{\beta^k}{k}\left[{}^a\!\log\frac{k}{m}\right]+q\sum_{x}^{\infty}\frac{\beta^k}{k},$$

where $[{}^a\!\log k]$ stands for the integer part of ${}^a\!\log k$.

Because we have

$$\sum_{x}^{\infty}\frac{\beta_k}{k}=-\frac{1}{x}-\frac{1}{x+1}-\ldots-\frac{1}{a\,(n+1)-1}+\sum_{a\,(n+1)}^{\infty}\frac{\beta_k}{k},$$

we have also

$$\left|\sum_{x}^{\infty}\frac{\beta_k}{k}\right|<\frac{a-1}{x}+\frac{a-1}{a\,(n+1)}<\frac{2a\,(a-1)}{a^q\,m},$$

consequently, if q, and at the same time x, tends to ∞, the product $q\sum_{x}^{\infty}\frac{\beta_k}{k}$ tends to zero, and we have established the result

$$C-\left\{C(m)-\frac{1}{m}\right\}=\sum_{am}^{\infty}\frac{\beta_k}{k}\left[{}^a\!\log\frac{k}{m}\right].$$

If we put here $m=1$, we obtain

$$C=\sum_{a}^{\infty}\frac{\beta_k}{k}\,[{}^a\!\log k].$$

and this expansion of the constant C, in which the integer a is arbitrary, is a generalisation of the series of VACCA, who only considers the case $a=2$, $\beta_k=(-1)^k$, and writes

$$C=\left(\frac{1}{2}-\frac{1}{3}\right)+2\left(\frac{1}{4}-\frac{1}{5}+\frac{1}{6}-\frac{1}{7}\right)+3\left(\frac{1}{8}-\dots-\frac{1}{15}\right)+$$
$$+4\left(\frac{1}{16}-\dots-\frac{1}{31}\right)+\dots$$

2. It is also possible to deduce in a more direct way the corresponding expansions of the coefficients C_h of the power series

$$\zeta(1+s)=\frac{1}{s}+C+\sum_1^\infty C_h\, s^h\,,$$

that for any value of s represents the RIEMANN function $\zeta(1+s)$. Supposing $s>0$ we have also

$$\zeta(1+s)=\sum_1^\infty \frac{1}{k^{1+s}}.$$

and as evidently

$$(1-a^{-s})\,\zeta(1+s)=-\sum_1^\infty \frac{\beta_k}{k^{1+s}},$$

we get the identical relation

$$1+C\,s+\sum_1^\infty C_h\, s^{h+1}=\sum_1^\infty \frac{\beta_k}{k}\left(\frac{sk^{-s}}{a^{-s}-1}\right).$$

Here we refer to the expansion

$$\frac{y\,e^{ty}}{e^y-1}=1+\sum_1^\infty y^h\,\bar{g}_h(t),$$

holding for $|y|<2\pi$ and for any value of t, in which $\bar{g}_h(t)$ stands for the polynomial

$$\bar{g}_h(t)=\frac{t^h}{h!}-\frac{1}{2}\cdot\frac{t^{h-1}}{(h-1)!}+\frac{B_1}{2!}\cdot\frac{t^{h-2}}{(h-2)!}-\frac{B_2}{4!}\cdot\frac{t^{h-4}}{(h-4)!}+\frac{B_3}{6!}\cdot\frac{t^{h-6}}{(h-6)!}-\dots,$$

involving the BERNOULLIAN numbers B_n.

For sufficiently small values of s we have therefore, putting $y=-s\log a$, $t={}^a\log k$

$$\frac{sk^{-s}}{a^{-s}-1}=-\frac{1}{\log a}+\sum_1^\infty s^h\,(-1)^{h-1}\,(\log a)^{h-1}\,\bar{g}_h({}^a\log k),$$

and finally we arrive at the equation

$$1+Cs+\sum_{1}^{\infty} C_h\, s^{h+1}=-\frac{1}{\log a}\sum_{1}^{\infty}\frac{\beta_k}{k}+$$

$$+\sum_{k=1}^{k=\infty}\frac{\beta_k}{k}\sum_{h=1}^{h=\infty} s^h\,(-1)^{h-1}\,(\log a)^{h-1}\,\bar{g}_h\,({}^a\log k).$$

But, as the righthandside is identically equal to a power series in s, we necessarily must conclude to

$$C_h=(-1)^h\,(\log a)^h\sum_{1}^{\infty}\frac{\beta_k}{k}\,\bar{g}_{h+1}\,({}^a\log k),$$

and especially to

$$C=\sum_{1}^{\infty}\frac{\beta_k}{k}\,\bar{g}_1\,({}^a\log k)=\sum_{1}^{\infty}\frac{\beta_k}{k}\left({}^a\log k-\frac{1}{2}\right).$$

For not specified values of a and k the probable value of ${}^a\log k-\frac{1}{2}$ is $[\,{}^a\log k\,]$; hence remembering that we already found

$$C=\sum_{a}^{\infty}\frac{\beta_k}{k}\,[{}^a\log k]=\sum_{1}^{\infty}\frac{\beta_k}{k}\,[{}^a\log k],$$

we may remark that the sum of the series

$$\sum_{1}^{\infty}\frac{\beta_k}{k}\left({}^a\log k-\frac{1}{2}\right)$$

is not altered, when ${}^a\log k-\frac{1}{2}$ is replaced by its probable value.

Botany. — *"The results of the temperature-treatment in summer for the Darwin-Tulip."* First part. (Communicated N⁰. 17, Laboratory for Plant-physiolog. Research, Wageningen, Holland.) By A. H. BLAAUW and Miss M. C. VERSLUYS.

(Communicated at the meeting of September 25, 1925).

§ 1. *Introductory, material and treatment.*

In the summer of 1922 and of 1924 bulbs of the Darwin-Tulip, Pride of Haarlem were exposed to 65 different combinations of temperatures in all between lifting and replanting. The results will be communicated in three parts: in the first and the second part the experiments of the summer 1922, in the 3rd those of 1924, which were based upon the results of the 1922-experiments. Finally in connection with the treatments in 1924 some test-experiments were made in the summer of 1925, the results of which cannot be published until 1926 in a 4th part. With a view to the cultures however we have thought best not to delay publishing the data hitherto found. Besides an occasional reference will be made to the detailed description: *"The periodical development of the Tulip"* by R. MULDER, which research will appear in some time as communication N⁰. 16.

The *material* supplied by C. G. VAN TUBERGEN of Haarlem, was sent to us directly after lifting and sorted, so that the experiments of 1922 could be started on July 20.

What the condition of the bulb is at that time, may be read in the above-mentioned research of R. MULDER. Here it will suffice to mention, that in July 20, 1922 at the beginning of the different temperature-treatments the greater number of the bulbs (save the scales with the reserve-food) had formed *2, 2 to 3, or 3 foliage-leaflets* (found in 12 of the 17 bulbs opened). As finally 4 to 5 foliage-leaves are formed, the experiments *after the lifting begin still in the leaf-forming period* (stage I). This is quite different from the Hyacinth, where as a rule the foliage-leafformation ends after the lifting, the growing-point is raised (stage II) and next is going to form the flower-cluster. (See 1920.)

These tulips were treated simultaneously with the first series of experiments on the Hyacinth (see 1924) and were initially considered as a provisionary experiment to find out, whether in a plant so closely related important differences might occur.

Just as the Hyacinth they were exposed to 1½°—5°—9°—13°—17°—20°—23°—25½°—28°—31° and 35°, 10 at a time for 2, 4, 6 and 10 weeks; after 2, 4 and 6 weeks they were placed in about 17° and next

10 weeks after the beginning of the experiments, these 11 × 4 = 44 groups each consisting of 10 experimental tulips, were planted ca 1 October.

Besides after 2, 4, 6 and 10 weeks 10 tulips were fixed in alcohol 96 % in order to trace the progress of leaf- and flower-formation and of the young bud in the 11 different temperatures during that time. These data will be discussed in the *second part.*

This being only an experiment for control and orientation, only 10 tulips were planted and the effect was traced till the flowering. Not until the third part data are given on the yield of new tulips.

§ 2. *The root-wall at the beginning of October.*

In the second part we shall discuss the events occurred during the summer, observed on bulbs fixed in alcohol, after 2, 4, 6 and 10 weeks and for convenience' sake we shall discuss in this first part, what is externally directly perceptible *after* those 44 temperature-treatments.

On planting, beginning of October '22 many points of difference were to be noticed in the condition of the *root-whorl.* The more or less advanced state of this root-wall was photographed and recorded by us independently, and from this a conclusion was drawn :

Furthest developed is the root-whorl after a treatment of *10 weeks in 13°*, when the roots already protrude from the root-wall. Next in progress are those groups, which have been exposed to 10 weeks 17°, 6 weeks 13° + 4 weeks 17° and 10 weeks 9°.

It is a striking fact that the root-whorl develops most rapidly in such low temperatures (low "celerrimum", see 1924).

The greatest contrasts appear, as may be understood, in the series remaining for 10 weeks in the 11 different temperatures. An impression of this is given in fig. 1, showing bulbs from those 11 temperatures photographed from below on one side at the beginning of October. Furthest developed is the root-whorl at 13°, next 9° and 17°, then 20°, 23°, 25½°, then 5° ; whilst at 28°, 31°, 35°, the root-wall is developed as little as at 1½°. The dry brown scale has been removed for the greater part in these bulbs in order to show the root-wall. From these bulbs one average type has been inserted in the photo-series. While 20°, 23° and 25½° are about equal, 25½° seems a little farther.

We intentionally say that in the low temperatures 9°—13°—17° a *celerrimal* (most rapid) development of the root-whorl takes place ; — we do not speak of an *optimal* development, for it may very well be, that in higher temperatures the development of the roots, though slower, is equally good or better with respect to the whole plant. That indication of most rapid (celerrimal) development, as in this case of the root-wall, is material with a view to the treatment for early flowering.

To this subject we shall revert, when treating the development of other organs.

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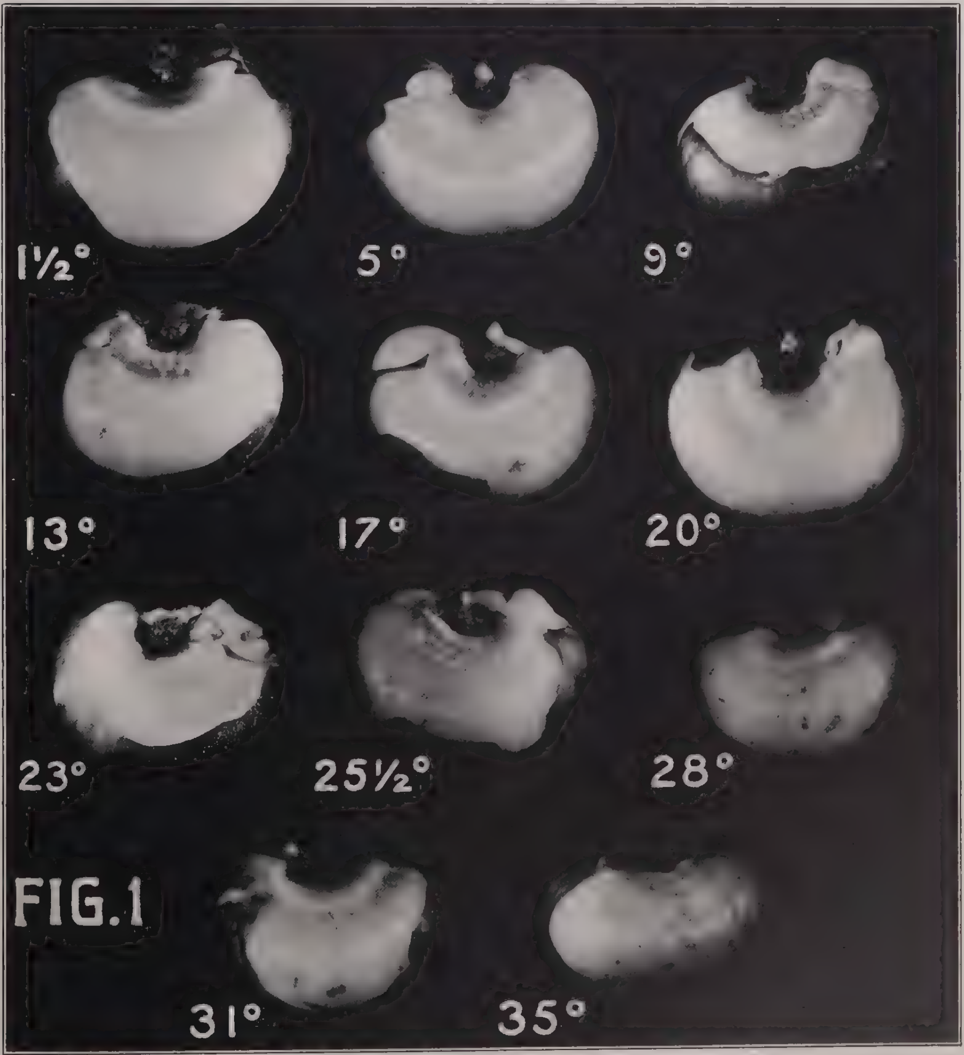

Fig. 1. Condition of the root-wall after a treatment for more than 10 weeks in 11 different temperatures.

§ 3. *Coming up.*

At the beginning of October 10 bulbs of each of the 44 treatments were planted in the open, 5 cms. deep and covered moreover with a layer of 4 to 5 cms. peat-dust. Next it was observed at different points of time which group appeared first i.e. stretched quickest. The winter (1922—1923) had been very mild.

Whilst the tulips, exposed to 10 weeks 5° (!) showed on January 4 already ca 3 cms. above the peat-dust and appeared quickest of all on Jan. 11, 4 of the 10 of the group 10 w. 1½° (!) showed just above ground, 9 of the 10 of 10 weeks 5° showed 4 to 5 cms. above the peat-dust, 4 of the 10 of the group 10 weeks 9° just appeared; a celerrimal stretching therefore in those groups which had experienced an uncommonly low temperature in the previous summer.

Table 1 clearly shows the condition on Febr. 11, 1925 after the peat-dust had been removed. According to the description made, the 44 groups have been given a successive number, denoting the advance in growth in length, which is in accordance with the order of succession of coming up in those weeks.

TABLE 1. Order of succession of coming up, on February 11, 1925.

Exposure	2 weeks	4 weeks	6 weeks	10 weeks
1½°	6	7	5	2
5°	7	6	3	1
9°	7	6	5	2
13°	8	7	6	4
17°	7	7	7	7
20°	8	8	8	8
23°	8	8	8	8
25½°	6	8	9	10
28°	8	8	9	10
31°	6	8	9	10
35°	8	9	10	10

N⁰. 1: 9—17 cms., N⁰. 2: 9—12 cms., N⁰. 3: 7—9 cms., N⁰. 4: 4—7 cms., N⁰. 5: 3—5 cms., N⁰. 6: 2—4 cms., N⁰. 7: 1—4 cms., N⁰. 8: ½—3½ cms., N⁰. 9: 0—3 cms., N⁰. 10: 0 cm., above ground.

We conclude that in spring on coming up (stretching) the *celerrimum* follows after an exposure to still lower temperatures than could be ascertained in Oct. with respect to the root-whorl.

This may be due either to the fact that stalk with leaves has a still lower celerrimal temperature than the root-system — or to the fact that celerrimum is found lower in the after-effect months later (February as contrasted with October).

Again the necessity is felt of distinguishing a *celerrimum* from an *optimum* in judging these intricate processes of the whole plant, for as we shall soon observe in description and photographs these plants (celerrimal as to stretching) had by no means had an optimal treatment.

§ 4. *Coming into bloom.*

After coming up the appearance of the flower and the coming into bloom was traced. Those different data on succession of coming up and flowering were recorded in detail for weeks together. A brief survey concerning the flowering will suffice here. For the progress of that growth and flowering after various treatments of the bulbs in the preceding summer a mild winter as the one of 1922—1923 is material. When bulbs variously treated are further cultivated not in a hothouse, but — as in our case — in the fields, and a long, continuous, severe winter follows, passing rather suddenly and late into warm spring-weather, many differences in more or less quick stretching and flowering due to an earlier temperature treatment are effaced, because after a long restraint owing to the winter, growth and flowering succeed rapidly in the various experimental groups. When however the winter is very mild, as was the case in '22-'23, or when the results of the experiments could be observed in a greenhouse where the bulbs were protected from frost, the difference of rate of growth and flowering are evident. And this is important, because they indicate to us the most suitable treatment for early flowering, which may require a treatment quite different from the optimum for the ordinary field-culture or especially for new bulb-formation. To this shall revert later on. It stands to reason, that the successive numbers, judged from 10 specimens, are only valuable as to their strong contrasts and that to differences for instance of 6 and 7 cannot be attached much value ; hence little irregularities occur, which would not have been expected otherwise ; it is doubtful whether they are valuable or not. But the chief points are without doubt directly to be read from this table 2. It should be remembered that all bulbs, kept in the 11 temperatures shorter than 10 weeks, were stored in 17° for the rest of the time. Hence the shorter they were kept in one of the other 10 temperatures, the slighter the influence was and the smaller the differences are.

1°. After a 2 weeks' stay it may be noticed, that the lower temperatures only slightly influenced the *rate* of flowering, that the higher temperatures (above 20°) are distinctly inhibitory. This is the after-effect of a 2 weeks' treatment after 8 months !

2°. Whereas the effect of 2, 4 and 6 weeks mutually shows but a very

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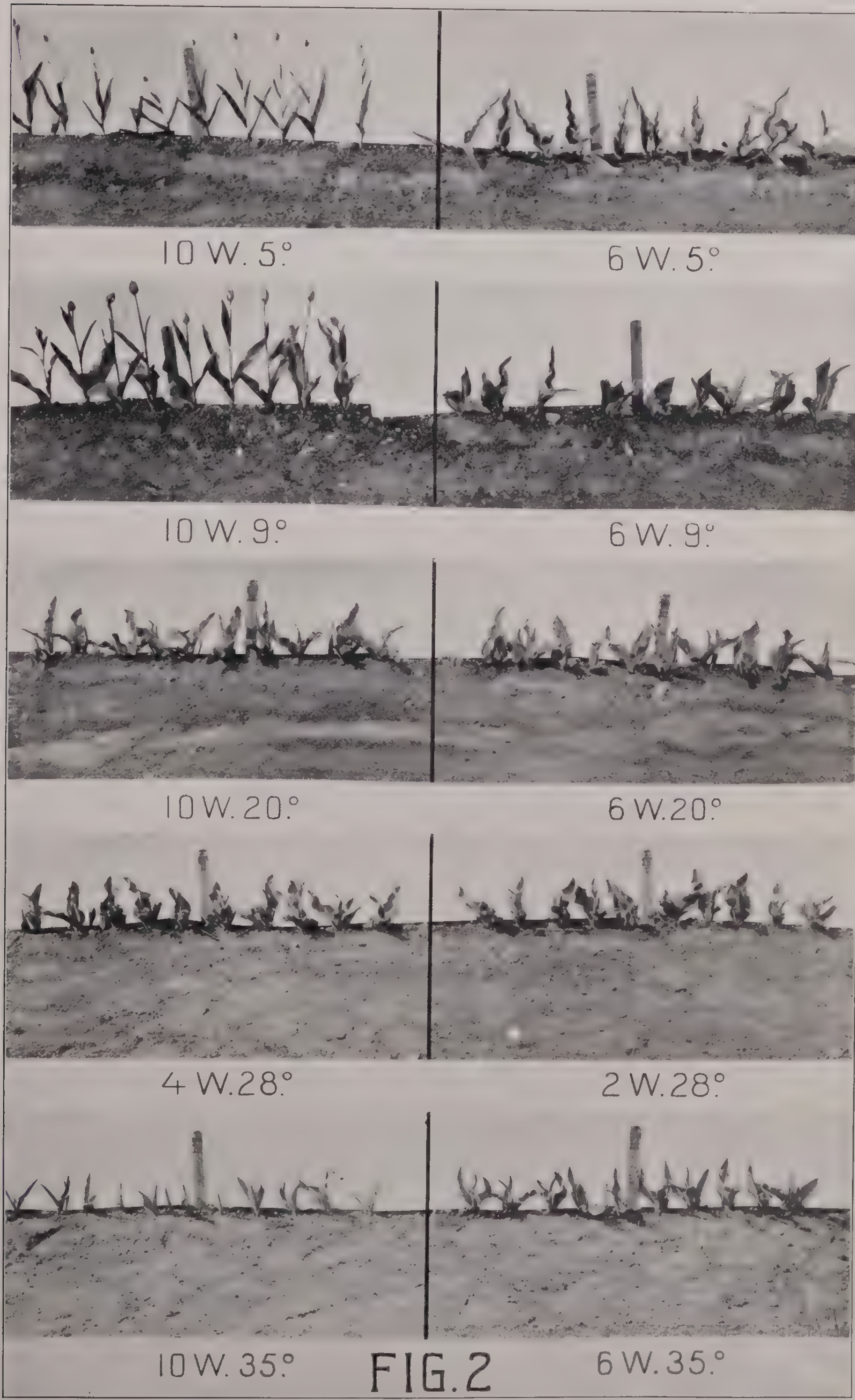
10 W. 5°
6 W. 5°
10 W. 9°
6 W. 9°
10 W. 20°
6 W. 20°
4 W. 28°
2 W. 28°
10 W. 35°
6 W. 35°

FIG. 2

Fig. 2. Photographs of a number of experimental groups on March 30, 1923 chiefly illustrating the earliest flowering groups and the different foliage.

TABLE 2. Order of succession of coming into bloom.

Exposive	2 weeks	4 weeks	6 weeks	10 weeks
1$^1/_2$°	6	6	6	3
5°	5	6	6	2
9°	6	6	5	1
13°	5	5	4	3
17°	5	5	5	5
20°	6	7	7	8
23°	7	7	8	9
25$^1/_2$°	7	7	8	10
28°	9	10	10	10
31°	9	10	10	11
35°	10	10	11	12

N⁰. 1 : April 17, all the 10 tulips flowering.
N⁰. 2 : April 17, 6 of the 10 tulips flowering.
N⁰. 3 : April 17, 1 of the 10 flowering.
N⁰. 10—12 : May 2, still closed.

slight difference, the treatment in the 6th to 10th week (month of September) is essential to the more or less rapid stretching and flowering, as is evident from the 4th column.

The first to flower were the Tulips, kept in 9° for 10 weeks and then planted in the fields. If this treatment is applied to the Hyacinth, not a single flower-cluster appears. From this the great difference between these closely related bulbs already appears. Even the greater number of those kept in 5° flowered on April 17 and must have finished their flower (see 2nd part § 10. fig. 3) in the ground after Oct. 1. Besides on April 17 a few of the continuous exposure to 1½° and 13° were already flowering. This as to the *celerrimum* of flowering; but it does by no means hold good for the *optimum* of flowering and of the plant as a whole.

This we shall see in considering the results of these treatments on plant and flower in a short report of the notes concerning them and in connection with some photos. (See fig. 2.)

As stated above, the differences show strongest in 10 weeks' continuous treatment. Starting from a specimen from *10 weeks'* 9° which was the first to open, we find fairly broad leaves with big flower-buds on March 30, whereas the experimental groups in 9° for a *shorter* time and especially in a temperature *lower* than 9° are less developed in a diminishing degree, partly as poor plants with narrower leaves and more deformed half green flowers, partly not even coming up at all (e.g. after 1½°).

We stated above and shall discuss later on (§ 10) that the flowers of 10 w. 1½° and 5° must have been formed partly (from 5°) or quite (from 1½°) in the ground after October. Though 10 w. 5° was the first to show above ground, 10 w. 9° was the first to open and excelled the poor plant of 5° far as to flower and leaf. The condition on March 30, '23 we find in fig. 2, from which it may be seen that shorter (than 10 w.) in 9° was sure to give later flowering, and lower than 9° a poorer plant.

Further the flowering falls the later according as the temperature in the previous summer was higher. This gradually decreases from 10 w. 9° to 20° and higher (conf. fig. 2 : 10 w. 9° and 10 w. 20° on March 30). But the foliage-leaves develop quite vigorously in the higher temperature, so that from 1½° to 25½° or 28° the foliage increases in breadth and grows more undulating; this is most conspicuous in the 10 weeks' treatment (5°—9°—20°—28°; conf. fig. 2). At 6 w. 5°—9°—20°—28° etc. (and next 17°) the contrasts have been effaced for a great part, so that it is evident how important the treatment in the month of September (i.e. in the last month before planting) is with respect to the rate of flowering and the development of the foliage. Above 25½°—28° the foliage diminishes, so that after a treatment with 10 w. 35° it is again poorer and not undulating. Then the plant is not only later, but also less favourable; in this case therefore we have not only passed a celerrimum, but also the optimum.

The lower temperatures, as 9° and 13°, may cause a loss in foliage-surface, but they promote a celerrimal development. That is material with respect to early flowering. But we shall revert to this point, because a more favourable combination of temperatures is possible (See 3rd part and the 4th part to be published next year).

Fig. 2 taken as early as March 30, gives a picture of the *celerrimal* treatment as to flowering (promoting early flowering). Some weeks after the groups from higher temperatures (20° and higher) are flowering likewise.

Several abnormal flowers, especially from highest and lowest temperatures, were fixed, but they require a detailed special morphological description, which we cannot enter into in this series of papers. To the kinds of abnormalities we shall briefly revert in the 2nd part (conclusion § 11).

As to flowering it is a very striking and surprising thing, that in those very earliest flowering specimens, exposed to 9°—17°, the number of floral organs is abnormally great compared to the normal monocotyledonous base 6 + 6 + 3, for perianth and stamens and the whorl of carpels. A more detailed discussion will be found in the following §.

§ 5. *The number of foliage-leaves and floral organs.*

We have accurately traced the number of foliage-leaves and floral organs, formed in a certain temperature. First of all we accurately counted and recorded the figures of the specimens (planted in the field) in April and May 1923. Afterwards the material fixed in alcohol during the treatment in the summer of 1922 was examined (See part 2). In so far as leaves or whorls of floral organs were ready as primordia, their number could be added to the figures of the specimens planted. From those numbers, found in April-May, only those were used, which referred to the bulbs that had surely formed the parts concerned in that temperature, — not therefore (in very low or high temperatures), when they had formed those parts afterwards in about 17° (after-treatment) or in the ground.

As mentioned before, the experiments were started on July 20, 1922 when 2 or 3 foliage-leaves had been formed. We add various tables on the number of leaves and floral organs, arisen during treatment in the temperatures mentioned (1st column), exclusively in so far as the leaf-series or a definite whorl of floral organs has been finished. Behind the temperature between brackets the number of weeks is found, after which this stage is reached. To give a direct picture of the variation in the number of the leaves or of the floral organs in their different whorls, the whole material is given first, i.e. how many times the number (e.g. 3, 4, 5, 6, etc.) of the organ concerned occurred. Next the number of observations (n), the average (M) and the mean error (m) have been given.

TABLE 3. Number of foliage-leaves.

Number:	2	3	4	5	6	7	8	n	M	m
$1^{1}/_{2}$° (10 w.)	—	3	3	**10**	0	1	1	18	4.78	±0.30
5° (6 w.)	—	7	9	**17**	5	1	—	39	4.59	±0.16
9° (2 w.)	—	13	15	**36**	8	1	—	73	4.58	±0.11
13° (2 w.)	2	7	10	**39**	17	3	—	78	4.91	±0.12
17° (2 w.)	—	15	13	**28**	18	2	—	76	4.72	±0.13
20° (2 w.)	—	14	21	**38**	6	—	—	79	4.46	±0.10
23° (2 w.)	—	14	16	**48**	2	—	—	80	4.48	±0.09
$25^{1}/_{2}$° (2 w.)	—	14	20	**43**	2	—	—	79	4.42	±0.09
28° (4 w.)	—	9	**29**	25	—	—	—	63	4.25	±0.09
31° (10 w.)	—	—	8	9	1	0	—	19	4.79	±0.22

Conclusions :

1°. after 2 or 3 foliage-leaves had been formed before July 20, the number was increased to 4 or 5 in all temperatures from 1½° to 31°, before the flower-formation begins. The rate, at which this happens, is very rapid with the temperatures 9°—25½° (within a fortnight), but grows much slower in the very low and very high temperatures. (See period in weeks between brackets.)

2⁰. The temperature has a very *slight* influence on the *number* of foliage-leaves still to be formed on the central growing-point. In the main the average number remains 4 or 5. Considering the great number of observations (n) in temperatures 9°—28° and the trifling mean error (m), the average values (M) may be relied upon, and it must be concluded, that after 20° and higher the formation of the average number of foliage-leaves is somewhat slighter than after exposure to 13° and 17°. The *slightly* higher figure after 10 weeks in 31° we shall not take into consideration on account of the small number.

Summarizing we recapitulate that the *number* of foliage-leaves, only partly formed, is influenced, but extremely little, by so diverging temperatures, that if we may accept some difference, the treatment in 13° may be considered to be among the most favourable as to the *number*. This in connection with what now follows on the number of floral organs.

In counting the *number of tepals* inner and outer whorl were taken together, as especially in the case of an increased number of floral organs they cannot be distinguished with certainty. In contingent transitional forms between foliage-leaves, tepals or stamens, which, considering the large number (n × the number of floral organs concerned) were not very numerous, the organ was added to that whorl to which it chiefly belonged according to its structure.

TABLE 4. Number of tepals.

Number	6	7	8	9	10	11	12	n	M	m
9° (6 w.)	—	4	5	**15**	9	4	—	37	**9.11**	±0.19
13° (4 w.)	—	3	10	**19**	**16**	7	**2**	57	**9.35**	±0.16
17° (2 w.)	2	15	**32**	13	10	3	—	57	8.40	±0.17
20° (2 w.)	**28**	18	**25**	2	2	—	—	75	7.09	±0.12
23° (4 w.)	**26**	19	14	0	0	1	—	60	6.87	±0.13
25½° (4 w.)	**38**	15	4	2	—	—	—	59	6.49	±0.10
28° (6 w.)	**29**	3	2	2	—	—	—	36	6.36	±0.14

Conclusions :

1⁰. Whilst the *number* of foliage-leaves still to be finished is but very slightly or scarcely influenced by the temperature, and the average number 4 or 5 is only finished in every temperature, before the growing-point is going to form the floral organs, the number of tepals is strongly influenced by the temperature in which the bulbs are stored, so that in 13° or 9° the average number of tepals originated is one and a half times the monocotyledonous base (2 × 3).

2°. From 13° to 28° the number of tepals decreases and approximates more and more the normal number 6, a figure rarely found after 9° and 13° (never in these experiments) and not prevailing until 25½° and especially 28°. (Higher and lower temperatures are not given, because e.g. in 5° and 31° after 10 weeks the flower-formation is not advanced far enough yet, and is not finished before the bulbs are planted in the open.)

3°. From the above and from the data on the number of foliage-leaves it likewise appears, that the increase in the number of tepals by no means occurs at the expense of the number of foliage-leaves.

We shall now mention in a similar way the *number* of *stamens*, combining likewise the inner and outer whorls and in the case of transitional forms adding these to the whorl which the structure of the organ resembles most. (See sub "number of tepals".) Though an increased number of tepals and stamens makes it hard to discover, which belong to the outer and which to the inner whorl or may be to a third whorl, it may be possible to decide this after more accurate, purely morphological studies. In these experimental morphological researches however, we have had to restrict ourselves to these conclusions.

TABLE 5. Number of stamens.

Number:	5	6	7	8	9	10	11	n	M	m
9° (6 w.)	—	2	6	9	**12**	6	—	35	8.40	±0.19
13° (4 w.)	—	—	9	14	**24**	8	2	57	8.65	±0.14
17° (4 w.)	—	4	16	**26**	8	2	—	56	7.79	±0.12
20° (4 w.)	—	22	**25**	10	1	—	—	58	6.83	±0.10
23° (4 w.)	1	**25**	**24**	9	—	—	—	59	6.69	±0.10
25½° (4 w.)	1	**29**	19	3	—	—	—	52	6.46	±0.09
28° (10 w.)	—	**17**	3	1	—	—	—	21	6.24	±0.12

Conclusions:

1°. We find here exactly the same phenomenon as with the number of tepals. The largest number of stamens is formed in 13° and also in 9°, though the average attained is slightly lower than in the case of the tepals.

2°. From 13° to 28° the average number gradually decreases, so that the *highest* temperatures approximate the monocotyledonous base 2 × 3 most in the average (M) and the actual number 6 is most frequent in this case (see especially 28°). In 13° it is never formed; in 9° in 2 of the 35 cases.

The figure 5, so "below normal", rarely occurs, probably without connection with the temperature employed, more as a "chance" deviation. Here we see it occurring twice (in 2 most favourable temperatures) with the stamens. Also after exposure to 31° and after Oct. 1 in the ground the figure 5 was found a few times in stamen- and tepal-whorl.

3⁰. The whorls of tepals and of stamens therefore are not increased in number of parts at the expense of each other, but the lower temperatures have this perfectly parallel effect on the whorls of these two organs.

In table 6 the *number* of *carpels* is given in a similar way.

TABLE 6. Number of carpels.

Number:	2	3	4	5	6	n	M	m
9° (10 w.)	—	7	**10**	1	1	19	3.79	±0.18
13° (4 w.)	2	18	**31**	2	—	53	3.62	±0.09
17° (4 w.)	1	**28**	**28**	—	—	57	3.47	±0.07
20° (4 w.)	1	**34**	21	—	—	56	3.36	±0.07
23° (4 w.)	—	**33**	24	—	—	57	3.42	±0.07
25½° (6 w.)	—	**27**	15	—	—	42	3.36	±0.08
28° (10 w.)	—	**16**	5	—	—	41	3.24	±0.10

Conclusions:

1⁰. In this case we have only to deal with one whorl, so normally 3 parts; hence the differences are not so striking as in tables 5 and 4. Besides it is possible, that as the effect on the stamen-whorls is a little less than on the tepals, the influence of this 5th whorl is still slighter than on the whorls lying more to the outside. Nevertheless the effect is perfectly parallel. It appears that the average number (sub M) at 9° and 13° is highest, and that considering the very slight mean error (m) of 0.07 to 0.10, doubtlessly the higher temperatures approximate the normal number 3 more than the low temperatures 9° and 13°.

2⁰. This is still more evident in the detailed figures in the preceding columns. At 9° and 13° the climax of variation is found with 4 carpels, at 17° there are just as many with 3 as with 4 carpels, at 20° and higher the climax falls at (the greater number has) 3 carpels.

3⁰. A few cases occur with 2 carpels, i.e. *below* the normal base, a most rare feature, likewise in the other floral whorls. In our opinion it has nothing to do with the continuous phenomenon we ascertained, viz. 'a great number of floral organs in lower temperatures', for it occurs here — in exceptional cases — as well, where the average is high (13° in 2 from the 53 cases, where there also occur 2 cases with 5 carpels).

It has become evident, that the greater number of floral organs in the lower temperatures is neither formed at the expense of the foliage-leaves, nor at their mutual cost, as e.g. in the case the flowers are double or full, when the inner whorls grow like tepals. (See the many cases described by K. ORTLEPP 1908 and 1915, and D. J. HILL 1766.) Every whorl increases its own number, especially at 9° and 13° most of all the outer whorls (tepals).

It was however not immaterial, to verify this parallel behaviour by every individual flower. For this purpose we give in table 7 a survey of the *sum of the floral organs,* which must normally amount or approximate the figure 15 (5 whorls of 3 organs).

TABLE 7. The whole number of floral organs.

Number:	15	16	17	18	19	20	21	22	23	24	25	n	M	m
9° (10 w.)	—	—	1	1	1	2	**5**	0	2	3	2	17	**21.59**	±0.58
13° (4 w.)	—	—	—	4	3	8	**10**	**13**	6	6	3	53	**21.55**	±0.26
17° (4 w.)	—	—	8	9	6	**16**	8	6	2	1	—	56	19.68	±0.24
20° (4 w.)	**17**	5	**10**	7	5	7	3	—	—	—	—	54	17.20	±0.27
23° (4 w.)	**18**	8	8	9	7	6	0	1	—	—	—	57	17.04	±0.25
25½° (6 w.)	**18**	7	12	9	1	0	2	—	—	—	—	49	16.53	±0.22
28° (10 w.)	14	3	1	0	1	2	—	—	—	—	—	21	15.90	±0.37

It appears, as was probable from the preceding, that likewise in the aggregate number of floral organs the same feature strikes the eye.

So the number of floral organs may be controlled with the temperature and experimentally by storing in 9° or 13° the number of floral organs may be increased far above the morphological base, and conversely by storing especially in 26° or 28° the base may be closely approximated.

§ 6. *On the combinations of the number of floral organs in the successive whorls.*

As the results discussed in § 5, which never occurred in the treatment of the Hyacinth (cluster) may be of interest for experimental morphology, we want to subject the figures in this paragraph to a closer examination. While 6 + 6 + 3 is the normal figure for the structure of the tulip, for the whole family of Liliaceae, and the base for the whole group of Monocotyledons, the question of the frequency of this combination presents itself, and likewise whether with a greater number of floral organs formed by low temperatures, there occur combinations more frequent than whatever other combinations.

For this purpose we have destined the combinations of these floral organs from the base $6 + 6 + 3$ up to and including $8 + 8 + 4$, i.e. the pure tetramerous tulip-flower. This includes 18 possible combinations (see the table subjoined). If we include combinations higher than 8 and 4 (carpels) the number of possibilities becomes much greater. Moreover the number of times that a certain combination occurs, becomes rarer and is restricted to the lower temperatures, in which a great number of varied combinations may occur. As to the tepals in 75 cases we find 2 flowers with 9, 2 with 10 after 20°, at 23° not any flower with 9, not any with 10 and one with 11 in 60 cases (tab. 4). As to the stamens in 20° only one of the 58 flowers has 9 stamens (tab. 5). More than 4 carpels have been found only a few times in 13° and 9° (tab. 6). Quite different from all others was one specimen exposed to 13° with 18 tepals, 21 stamens, 10 carpels! We did not insert this specimen in the preceding tables.

Let us therefore abide by the 18 combinations 6—6—3 to 8—8—4.

334 of the 539 flowers, (from fixations and field-experiments) which after 44 different temperature-treatments could be examined, belong to these 18 combinations. In a perfectly equal division (without preference) each of these combinations should have 18, 55, i.e. 18 or 19 flowers. We find however as summed up in table 8.

Conclusions :

Certain combinations of figures are surely more frequent in the whorls of floral organs than others ; conversely there are certain combinations rarely or never occurring. In the second column of table 8, which is the principal, all flowers belonging to these combinations have been recorded, so not only those formed in one temperature, but also those formed partly in e.g. 5° and then 17°, or 5° and later outside in the field, etc. In the 7 following columns the same has been given in detail for those flowers which have certainly been formed in 9°, 13°, etc. Their number amounts to 217 out of 334 ; no special columns have been given of the remaining 117 formed in different temperatures (e.g. 4 w. 5° + 6 w. 17°, 6 w. 5° + 4 w. 17°, 10 w. 5° + outside in the field, etc.), because in that case the number per column would grow very low and a conclusion could scarcely be drawn.

1°. On our observing the second column, it is at once apparent, that the base 663 is not arbitrary, but quite frequent, that 884 is no more a combination as accidental as e.g. 683 or 864, etc., but that after 663 it has a much greater chance of originating than other combinations ; next 773 is rather frequent ; then 774 and fairly often 873 and 874.

2°. Some combinations as 683, 684, 864 are — at least in these 44

TABLE 8. Number of flowers occurring in 18 different combinations of numbers of floral organs.

Numbers of tepals stamens, carpels	Number per combination of 334 flowers from all exposures together	Formed in 9°. The 17 remaining flowers occurred in combinations with higher fig.	Formed in 13°. The remaining (28) with higher figures	Formed in 17°; 32 with higher figures	Formed in 20°; only 5 are exceptions to these combinations	Formed in 23°; only 2 exceptions	Formed in $25^{1}/_{2}$°; 4 exceptions	Formed in 28°; 1 exception
663	**84**				18	18	17	14
664	9				1	2	1	2
673	15				3	3	5	
674	9				2	1	4	
683	1			1				
684	0							
763	19			1	1	2		
764	5					1	1	1
773	**33**	1	0	5	6	6	7	1
774	**27**		2	0	4	7	6	
783	7		1	2	1	1	1	
784	4			1	0	1		
863	12			3	2			
864	1							
873	23		1	4	1	2	2	
874	24		2	2	5	4	1	
883	12		1	1	1	1	0	1
884	**49**	1	3	14	6	6	0	1
Number	334	2	10	34	51	55	45	20
Chance per comb. (round numbers)	19	(1)	(1)	2	3	4	3	2

temperature treatments — extremely rare or even never occurring. So we may communicate here (see part 3) that *in 883 flowers exposed in 65 different modes, the combination 684 has never occurred.*

3⁰. On our considering the frequency of these combinations further in connection with the temperature applied, taking into account only those flowers, which have positively been formed *in* that temperature (9° to 28°), we see how much the origin of a certain combination is due to that exposure. *The combination 663 is the most frequent* — that is *only in exposure to 20° and higher ;* at 17° and lower this combination never or very seldom occurs (see part 3). *After exposure to 17° the combination 884 is most frequent,* but never or rarely occurs after 25½° and upwards, whilst an exposure to 13° and 9° yields figures for most of the flowers, exceeding those of these 18 combinations. The intermediate combinations 773 and 774 are most frequent in (17°), 20°, 23°, 25½°, and are rarely formed by a higher temperature (28°) or lower temperatures.

So experimental morphology teaches us, that in the case of the Tulip the pure monocotyledonous base (663) greatly depends upon definite temperatures, and that we are capable of fairly eliminating this base through temperatures below 20° and of forming e.g. by exposure to 17° a rather high percentage of tetramerous tulip-flowers (ca 21 % of the flowers formed in 17° were purely tetramerous).

4⁰. In 6 of the 18 combinations, i.e. 33 %, tepals and stamens occur in equal numbers, which may give rise to a very regular arrangement in the primordia. Now the question is, whether the number of flowers containing an equal number of tepals and stamens exceeds 33 %. It appears, that 214 of the 334 flowers, therefore not 33 % but 64 %, are among these 6 combinations, so that *there exists a preference for an equal number of stamens and tepals,* at least with the figures 6, 7 and 8.

§ 7. *Is for instance the tetramerous flower a passing result of the temperature?*

The question immediately rises whether certain combinations, e.g. pure tetramerous flowers, preserve this feature more or less in the young bulbs, formed by these bulbs, i. e. whether the feature is transmitted as a property to the lateral buds, likewise when the vegetative descendants are exposed next year to a temperature-combination, closely approximating the base 6—6—3.

To solve this question a crop of tulips, yielding purely tetramerous flowers (8-8-4) in May 1924, was lifted in July and from this crop 48 bulbs of main buds and 124 largest bulbs of the more advanced lateral buds were stored for 7 weeks in 26° + 4 weeks in 17°. The 48 main-bud-bulbs yielded 70 flowers.

Several of them yielded more than one flower-stalk, which is rather striking, considering it had occurred only 5 times in the 440 bulbs treated in 44 modes.

101 of the 124 largest more advanced lateral buds gave one flower-stalk. In May 1925 the following combinations occurred :

In the 70 flowers from main-bud bulbs		In the 101 flowers from the further lateral buds	
6—6—3	**48** times	5—6—3	1 times
6—6—4	4 „	5—7—3	1 „
6—7—3	7 „	6—5—3	1 „
6—7—4	3 „	**6—6—3**	**91** „
7—6—4	1 „	6—6—4	4 „
7—7—3	2 „	8—8—3	1 „
7—7—4	3 „	8—8—4	1 „
8—8—4	2 „	12—10—?	1 „

So 139 of the 171 flowers (on bulbs, vegetatively descendant from bulbs with purely tetramerous flowers) showed the combination 6-6-3 and only 3 the combination 8-8-4 after an exposure to 7 w. 26° + 4 w. 17°.

It is evident, that *the number of floral organs again depends upon the the temperature every year* and there is no question at all of making the property permanent in the bud (the future new bulb). This however has nothing to do with the question whether by mututal pollination, i. e. generatively, the tetramerous condition is more or less maintained ; this however is not probable.

Finally we mention one purely pentamerous tulip (10—10—5) in our grounds in 1924. The bulbs yielded by this were also exposed to 26° (7 w.) and 17° (4 w.) In 1925 only the main-bud-bulb gave a flower purely trimerous.

The literature cited will be mentioned at the end of the third part.

September 1925.

Physics. — *"On a misconception in the probability theory of irreversible processes"*. By Mrs T. EHRENFEST-AFANASSJEWA.

(Communicated at the meeting of June 27, 1925).

Often it is thought that the two following statements contradict each other:

STATEMENT I. *A given course of a mechanical system with very many degrees of freedom is as probable as the contrary course,* and

STATEMENT II. *From every state which is not the most probable, the system tends with great probability toward the most probable state.*

This impression really is false and arises from the *confusion* of two statements, *both equally true,* as will be shown in what follows by means of a simplified scheme. — Consider a continuous series of discrete points lying in a plane with all integers (positive and negative) as abscissae, and with ordinates H which comply with the following conditions:

1. The ordinates are positive integers between $H_{min} = 0$ and $H_{max} = H_m$.
2. The successive ordinates always differ by 1.
3. The various values of the ordinates have different probabilities (i. e., appear although infinitely often yet in differing proportions), and this probability increases from above to below. (Thus the ordinate $H = 0$ has the greatest and the ordinate H_m the least probability).

A point whose ordinate is greater than those of the two adjacent ones we will call a "peak"; a point whose ordinate is less than those of the two adjacent ones, a "valley". — The succession of two points shall be called a "descending slope" whenever the point with the smaller abscissa (the beginning") has a greater ordinate than that with the greater abscissa ("the end"). In the contrary case we shall call it a "rising slope". — We shall say that our curve "rises" at a point P whenever it is the beginning of a rising slope; if the point P is the beginning of a descending slope we shall say that the curve "descends" at this point.

Now let us ask two questions:

QUESTION A. Given a certain height H. How great is the probability $W(H \rightarrow (H-1))$ that the curve descends at this point? — This probability, as may easily be derived from property 3 [1]) is greater than $^1/_2$ for all values of H that differ from zero. For $H = H_m$ it is equal to 1, for all points at a height $H = H_m$ are peaks. But for $H = 0$ it is equal to 0, for at this height all points are valleys. — Consequently it follows, that for points at every height $H \neq 0$ the probability $W(H \rightarrow (H+1))$ that the curve rises there is less than $\frac{1}{2}$. Thus we obtain:

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[1]) Cf. PAUL und TATIANA EHRENFEST. Ueber zwei bekannte Einwände gegen das Boltzmannsche H-Theorem. Phys. Zschr. 8, 1907, 311.

THEOREM A. For all heights except $H=0$ the probability that the curve descends is greater than that it rises.

QUESTION B. To compare the probability of a descending and a rising slope between the same two heights H and $H-1$. — The answer is:

THEOREM B. The probability for a descending and a rising slope between two particular heights H and $H-1$ are equally great.

We see this by asking how a certain height H which just has been reached at a point P can again be reached at a point P'. This can occur if the point P is the beginning of a raising slope $H \rightarrow (H+1)$, and then necessarily the point P' is the end of a descending slope $(H+1) \rightarrow H$, for we consider the point P', at which, after point P, the height H is reached for the first time, in which case the height $H-1$ is not reached at all between the points P and P'; or if point P is the beginning of a descending slope $H \rightarrow (H-1)$ and P' the beginning of a rising slope $(H-1) \rightarrow H$, in which case neither of these two particular slopes can occur more than once between P and P'. We also notice that point P' can not be missing from our curve, for each height between H_m and O is reached infinitely often.

Thus in any finite part of our curve the count Z_I of the slopes $H \rightarrow H-1$ and Z_{II} of the slopes $H-1 \rightarrow H$ must be the same or differing by no more than one, and in the limit for $Z_I = \infty$ is $\frac{Z_{II}}{Z_I} = 1$. That is to say, the probabilities for the two slopes are the same.

What relation then exists between the two theorems A and B and the two statements I and II? What frequently is not perceived properly is that statement II is a consequence of theorem A while statement I is not directly connected with theorem A, but is a consequence of theorem B. — The two statements I and II clearly are conflicting with each other as little as the two theorems A and B. — However, since the occurrence side by side of I and II is often considered a paradox, we shall consider further how theorem B depends on A.

The probability of a descending slope $H \rightarrow (H-1)$ is the product of two probabilities: the probability $W(H)$ that the beginning lies at the height H, and the probability $W(H \rightarrow (H-1))$, that the curve descends at that point.

The probability of a rising slope $(H-1) \rightarrow H$ is the product of two others probabilities, $W(H-1)$ that the beginning lies at the hight $H-1$, and $W((H-1) \rightarrow H)$ that the curve rises at that point.

Thus from (3) it follows:

$$W(H) < W(H-1)$$

and from theorem A:

$$W(H \rightarrow (H-1)) > \tfrac{1}{2}$$
$$W((H-1) \rightarrow H)) < \tfrac{1}{2},$$

thus

$$W(H \rightarrow (H-1)) > W((H-1) \rightarrow H).$$

It is thus quite easily possible that the two products

$$W(H) \,.\, W(H \rightarrow (H-1))$$

and

$$W(H-1) \,.\, W((H-1) \rightarrow H)$$

are equally large. However, the topological considerations above must be taken as the rigorous proof of this equality.

Attention may also be called to the following: the quasi-periodic return of the ordinates of our curve to each value assumed once occurs only by definition (1, 2, 3) and is independent of the sort of phenomenon of which it is taken as an image.

Leiden, May 1925.

Anatomy. — C. J. VAN DER HORST : *"The Cerebellum of fishes. I. General morphology of the cerebellum.* (Central Institute for Brain research. Amsterdam). (Communicated by Dr. C. U. ARIËNS KAPPERS.)

(Communicated at the meeting of September 26, 1925).

Concerning the general structure of the cerebellum of fishes three quite different lines of development can be distinguished which in their final stages, as found in Selachians, Chondrosteans and Teleosts, deviate to such a degree that it makes a direct comparison of these cerebella very difficult and has been the cause of erroneous interpretations.

To comprehend the development and morphological significance of the different parts of the cerebellum of fishes it is necessary to begin with a simple shaped and yet well developed cerebellum like that of Ceratodus. This cerebellum has been fully described by HOLMGREN and VAN DER HORST. It has practically the shape of a thick plate, but for a ridge in its middle part which protrudes downward into the fourth ventricle, and extends almost the total length of the cerebellum. It is rather flat in longitudinal direction but in crosssection it is crescentshaped, which is especially apparent in the middle part, at the level of the entrance of the trigeminus. Here two longitudinal furrows, one at the side of the ventricular and one on the outer surface, clearly indicate the boundary between the cerebellum and the oblongata. The granular mass is found at the side of the ventricle over the whole breadth of the cerebellum at this level, whereas the outer surface wholly consists of molecular matter.

The caudal border of the cerebellum of Ceratodus is convex. In crosssection the cerebellum has here the shape of a flat plate consisting of a granular and a molecular layer, which covers the fourth ventricle. On both sides this plate is connected with the dorsal border of the oblongata by means of the choroid membrane. Further frontad this plate is more and more curved until its edges fuse with the dorso-lateral margins of the oblongata. Where the fusion takes place, the granular mass curves outward and in this way the small but well defined auricles are formed.

The granular mass of the auricle continues in a caudal direction, though it can be clearly distinguished from it, into the lobus liniae lateralis anterior. This lobe forms the most dorso-lateral part of the oblongata and extends in a caudal direction to about the level where the first vagus roots leave the brain. I consider it better to call this nucleus which belongs to the dorsal root of the anterior lateral line nerve lobus liniae lateralis dorsalis and I will do so in this article. At the ventral side of this dorsal lobe the crista cerebellaris is found, which stretches far more in caudal direction than the lobe. At the frontal end it continues with the molecular layer of the cerebellum. The lobus liniae lateralis posterior is situated ventral to the crista, being the nucleus of the N. lateralis posterior and also of the ventral root of the anterior lateralis. Herefore I think it is better to call this nucleus lobus ventralis.

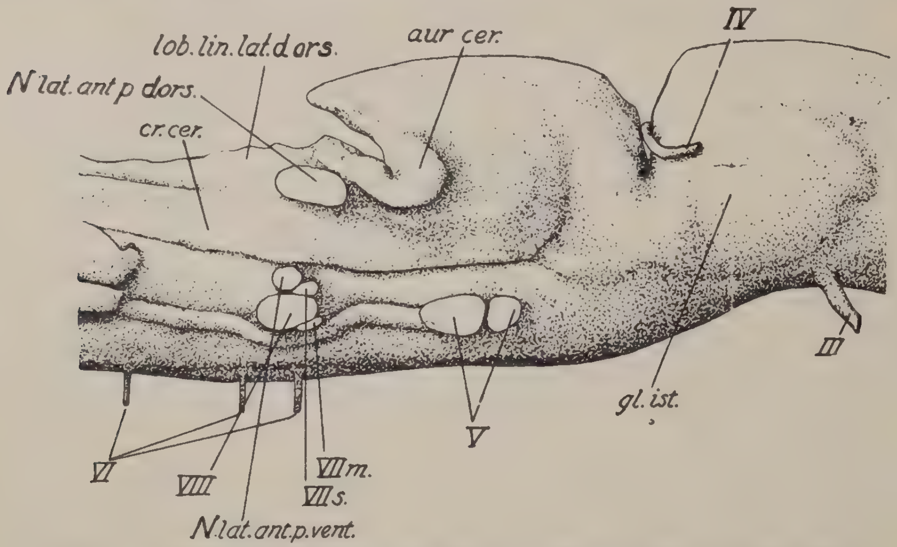

Fig. 1. Cerebellum and medulla oblongata of Ceratodus from the lateral side. After HOLMGREN and VAN DER HORST.

In the frontal part of the cerebellum on both sides of the ventricle the granular layer becomes considerably thicker and the molecular layer at the outside becomes gradually thinner. Finally the granular mass reaches the surface of the lateral sides of the cerebellum, so that the molecular layer forms then only the dorsal surface. The lobus liniae lateralis ventralis is connected with this lateral granular mass, and this mass continues in a frontal direction along the lateral side of the midbrain to the level where the oculomotorius leaves the brain.

In the chapter about the cerebellum, principally compiled by me, HOLMGREN and VAN DER HORST identified this lateral granular mass with the ganglion isthmi. It is possible that the frontal part, covering the lateral side of the midbrain, is homologous with the ganglion isthmi, but the caudal part of this granular mass, situated in the frontal part of the cerebellum, certainly can not be identified with this ganglion. It is the eminentia granularis of teleosts, as will be explained later on. In the meantime I will call this granular mass in this article the eminentia granularis.

Because of the fact that the dorsal lateralis nucleus is connected with the auricle and the ventral lateralis nucleus with the eminentia granularis, it follows, that these two parts of the cerebellum have a similar function. Especially does HERRICK call attention to this fact, but because of this functional similarity HERRICK did not see the morphological difference between these parts. According to him the eminentia granularis is homologous with the auricle.

In connection with this I should call attention to the fact, that in Ceratodus the two frontal lateralis roots exchange a great number of fibers, before they enter the brain. In this way the functional similarity between auricle and eminentia granularis is still increased. The only difference is, that the ventral lateralis nucleus is in close connection with the nucleus of the N. octavus, even to such an extend that it is impossible to distinguish these two nuclei.

The auricle belongs almost wholly to the area of the N. lateralis, whereas the eminentia granularis is not only in connection with the lateralis but also with the octavus. On the other hand the middle part of the cerebellum is principally the endnucleus of secundary tracts arising from the mesencephalon or which ascend from the spinal cord and the oblongata and which carry somato-sensory stimuli.

Starting from such a simple and yet well developed cerebellum, as is found in Ceratodus, it is possible to understand the morphological significance of the different parts of the cerebellum, as it has developed in different directions in the other orders of fishes.

In Selachians we find the middle part, the corpus cerebelli, enormously developed and the same is the case with the auricles, as has also been explicitly described by VOORHOEVE for a great number of sharks and rays. The auricle extends frontad along the total length of the cerebellum, so that the place, where the eminentia granularis might be expected, is covered by the auricle. In embryo's, in which the auricles are still smaller, the eminentia granularis is plainly visible, but during further development it is included more or less within the auricle. So we see, that the lobus liniae lateralis ventralis of Selachians is connected with the auricle, namely with the frontal part of it. But I will not enter into details here about the morphology of the cerebellum of Selachians.

Whereas the cerebellum of Selachians, upon becoming too large to form a flat plate, curves upwards in the middle part, in Crossopterygians it curves downwards in the ventricle (VAN DER HORST). In the median sagittal plane the skull cavity deeply penetrates into the cerebellum, so that the two lateral halves, forming the cerebellum, are connected in these fishes only by the ependyma and a thin layer of crossing fibers.

In Chondrosteans (Acipenser, Polyodon) the cerebellum is formed principally in the same manner, but for a few differences, by which this curving inwards of the cerebellum is less striking in Chondrosteans than in Crossopterygians. The main difference in this respect is, that the median fissure which remains in Crossopterygians between the two lateral halves of the cerebellum, disappears in Chondrosteans for the greater part, so that the curved in part is almost a solid mass. The second difference is, that the auricles in Crossopterygians are very small or lacking altogether, whereas in Chondrosteans they are very large and furthermore they are situated far dorsally, so that they cover the lateral surface of the corpus cerebelli. So when comparing Chondrosteans with Teleosts one gets the impression, that the corpus cerebelli is not curved inwards into the ventricle, but only that the auricles are situated far dorsally.

This dorsal position of the auricles is a result of the curving inwards of the cerebellum. This makes it necessary for the ventricle to enlarge, and this enlargement occurs by the stretching out of the lateral sides of the fourth ventricle in a dorso-ventral direction. This becomes clear upon comparing fig. 2 of Calamoichthys, showing a section slightly caudal of the cerebellum, with fig. 3 of the same animal showing the most caudal section, in which the corpus cerebelli is connected with the dorso-lateral border of the oblongata.

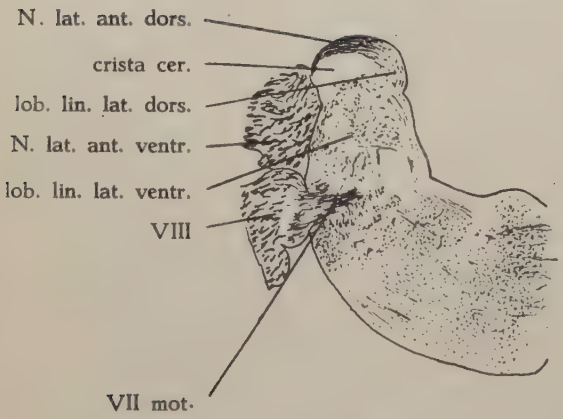

Fig. 2. Calamoichthys calabaricus.

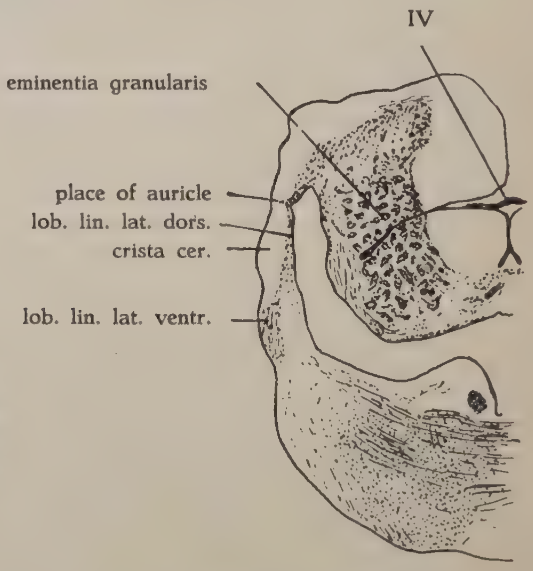

Fig. 3. Calamoichthys calabaricus.

Figure 4 shows a similar section of the brain of Polypterus and here we see a striking difference between the two Crossopterygians. In Polypterus the granular mass reaches the lateral surface at the place, where the caudal border of the cerebellum unites with the dorso-lateral margin of the oblongata. Here a distinct, though small, auricle is present. The choroid plexus had been removed from this brain, so that the lateral recess, that otherwise covers the auricle externally, is not visible in the sections. On the other hand in Calamoichthys the auricle is lacking absolutely, the crista cerebellaris being directly combined with the molecular layer of the cerebellum.

This slight development or total absence of the auricle in Crossopterygians is in close relation to another remarkable fact. In Chondrosteans and

Selachians, as in Ceratodus, the dorsal root of the lateralis anterior is much thicker than the ventral root. But in Crossopterygians the dorsal root is small and the greater part of the lateralis fibers enters ventrally (fig. 2). So we see, that the dorsal lateral line lobe in Crossopterygians is relatively much smaller than in the other fishes mentioned above. And as the auricle is in close relation with the lobus liniae lateralis dorsalis, we need not be surprised, that also the auricle is here very small, or absolutely wanting. It is not necessary that this reduction of the dorsal lateralis root indicates, that the whole lateral line system in less developed in Crossopterygians, and as we will see still more in Teleosts, than in Chondrosteans and Selachians. As I mentioned above, in Ceratodus an important exchange of fibers is found between the two roots of the anterior lateralis before they enter the oblongata. In Crossopterygians the small dorsal root combines with the large ventral root directly outside the brain. It is quite certain, that fibers entering dorsally in Chondrosteans and Selachians will do so ventrally in Crossopterygians.

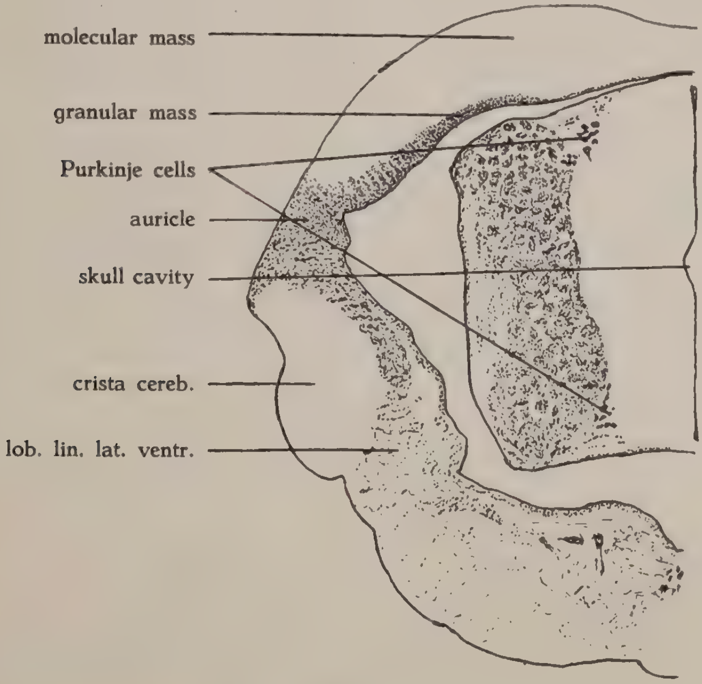

Fig. 4. Polypterus bichir.

The eminentia granularis of the Crossopterygians and Chondrosteans has shifted in dorsal direction in the same way as the auricle. We find this eminentia quite at the dorsal surface of the cerebellum and in Crossopterygians it reaches the surface even in the median fissure. In Chondrosteans the eminentia is more distinct than in Crossopterygians.

A third line of development of the cerebellum is found in Holosteans and Teleosts. We find the most simple condition which is easiest to be compared with that of Ceratodus in Amia. I was unable to obtain suitable material of Lepidosteus. The cerebellum of Amia shows principally the same structure as that of Ceratodus. It covers as a curved plate the frontal part of the oblongata. The caudal border is convex and forms here the roof of the fourth ventricle. Also the ependyma, forming a distinct lateral recess, is attached in the same place as in Ceratodus.

Whereas in Ceratodus the freely projecting caudal part of the cerebellum consists of an outer molecular and an inner, ventricular, granular layer, this caudal part in Amia is formed only by molecular substance (fig. 5). Only at the ventricular side and especially near the attachment of the ependyma scattered granular cells are found between the fibers. When studying the brain from this level in frontal direction, we see that soon a real granular mass appears in the sections (fig. 6), not at the ventricular side but in the middle of the molecular mass. The molecular substance situated at the dorsal side of this granular mass is the same as found in Ceratodus, whereas the ventral molecular mass consists of crossing fibers arising from the crista and forming the tractus vestibulo-cerebellaris. The fact, that groups of granular cells are scattered between the fibers shows, that the fibers have pushed away the granular substance, which was situated originally at the ventricular side.

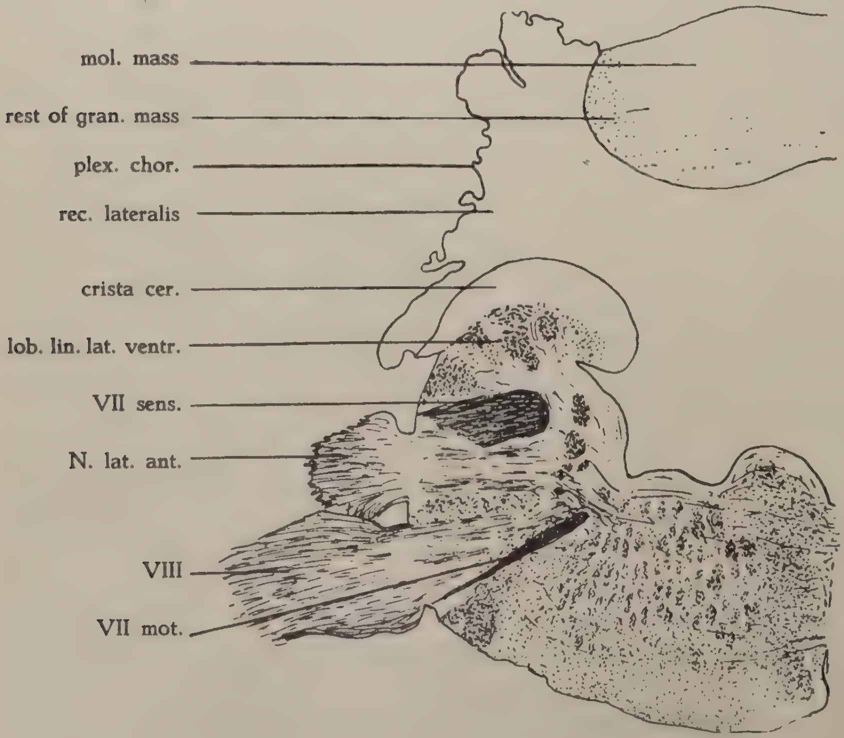

Fig. 5. Amia calva.

Running from the crista to the cerebellum the fibers curve in caudal direction to cross over near the caudal border of the cerebellum. So we see, that the ventral molecular layer soon splits, in the median sagittal plane, into two parts (fig. 6), which, running in a frontal direction, are separated more and more. The two parts disappear wholly at the level, where the molecular mass combines with the crista cerebellaris (fig. 7).

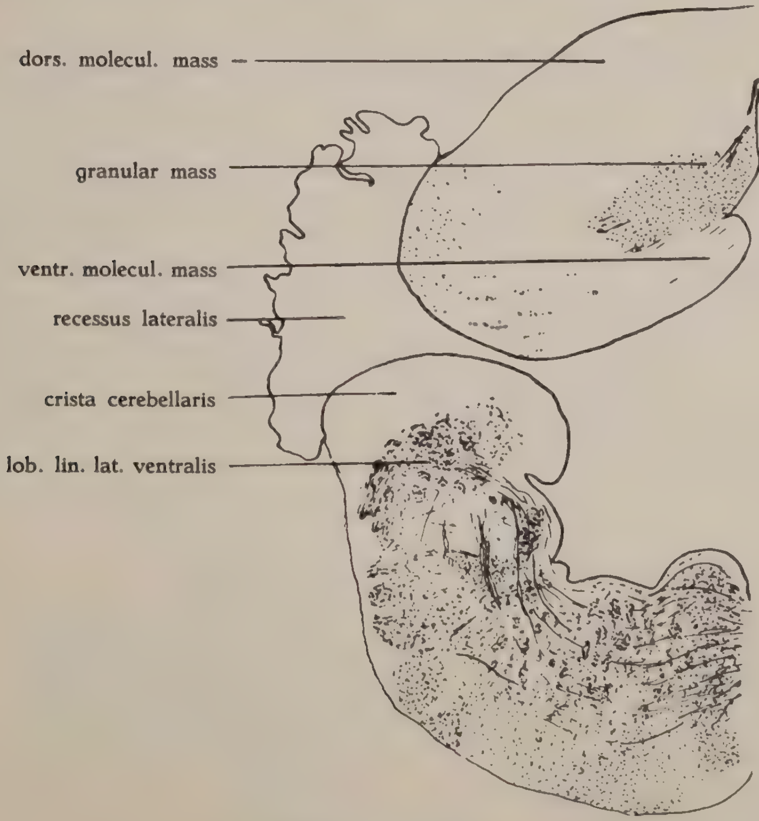

Fig. 6. Amia calva.

Because the vestibulo-cerebellar fibers run from the crista along the ventricular side of the cerebellum and here push away the granular substance, it goes without saying, that an auricle cannot be present. Only the granules that are scattered through the whole ventral molecular mass, are a little more densely packed at the place, where cerebellum and oblongata unite and where the auricle might be expected. This accumulation of granules may be looked upon as a rest of the auricle. In Amia only a few granular cells are found here, in some Teleosts, e.g. Esox, by far more. The granules may also form a small compact group like in Osmerus (fig. 9).

As mentioned before, the dorsal root of the lateralis anterior is much smaller than the ventral root in Crossopterygians. This root is absolutely lacking in Amia and Teleosts. All lateralis fibers enter ventrally to the crista cerebellaris (fig. 5). Berkelbach van der Sprenkel mentions a dorsal root of the lateralis anterior in Silurus, but this root is a bundle of fine lateralis fibers, forming the most frontal part of the entering nerve

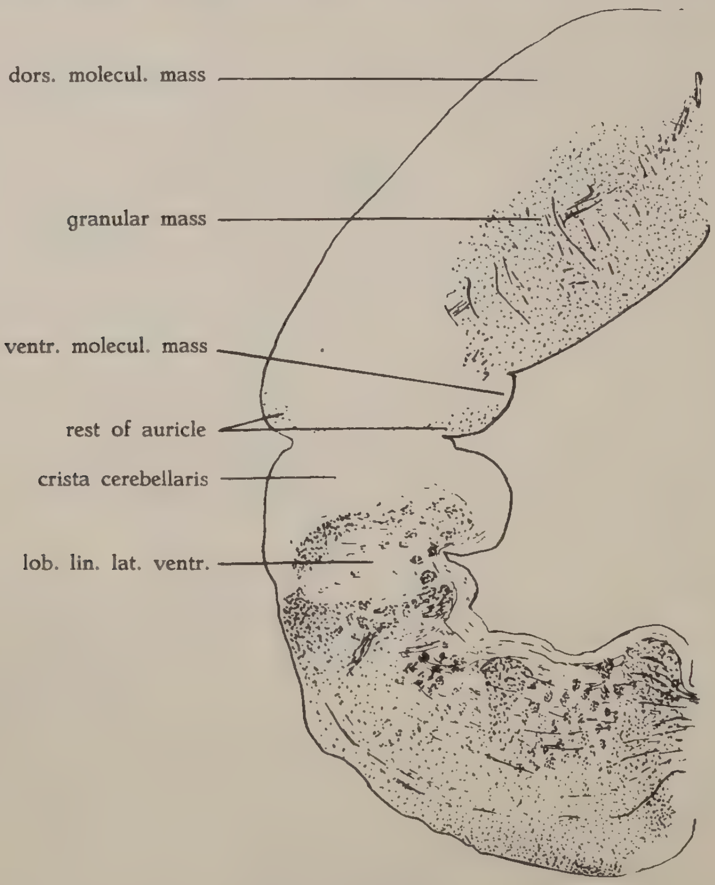

Fig. 7. Amia calva.

and ascending directly to the cerebellum. The fact that this ventral root consists of coarse and thin fibers, makes it apparent that the dorsal lateralis root is inserted in the ventral root in Teleosts.

According to SCHEPMAN in Cyclostomes the dorsal root consists only of coarse fibers and the ventral of thin ones, whereas in Teleosts both types of fibers occur in the ventral root.

If we continue our study of the cerebellum in Amia in a frontal direction, we see that the granular mass extends more and more in lateral direction, untill finally it reaches the lateral surface of the cerebellum. In figure 8 the granular mass is still covered by a thin layer of molecular substance, but this layer disappears a few sections more frontally. Here we find the molecular layer only at the external surface of the middle part of the cerebellum or the corpus cerebelli. The lateral mass of granular substance, found in the same way in Teleosts (fig. 11), has been described by FRANZ as eminentia granularis. In Ceratodus this lateral extention of granular substance occurs in quite the same way. So here it ought to be called also eminentia granularis. The ventral lateralis nucleus passes over into this eminentia granularis.

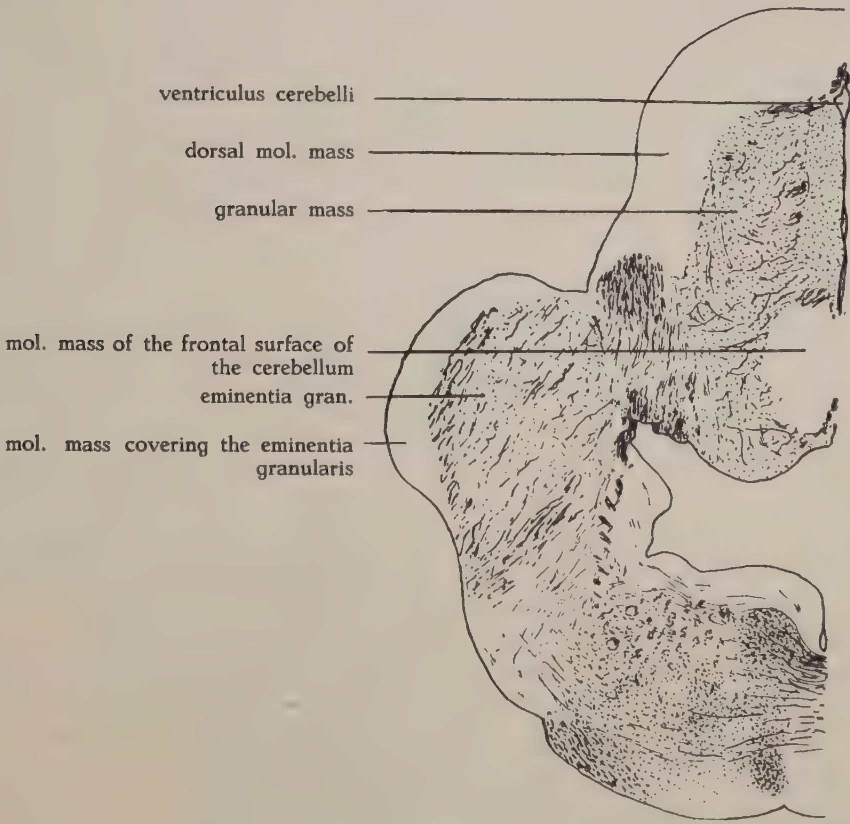
ventriculus cerebelli
dorsal mol. mass
granular mass
mol. mass of the frontal surface of the cerebellum
eminentia gran.
mol. mass covering the eminentia granularis

Fig. 8. Amia calva.

In the frontal part of the cerebellum the two eminentiae granulares are connected by a band of granular cells, which, situated along the roof of the fourth ventricle, form the most ventral part of the corpus cerebelli. In Amia the eminentiae can be clearly distinguished from this band of granules. In this fish the frontal extremity of the eminentia is seen some sections in front of that figured in fig. 8, whereas the band of cells above the ventricle reaches farther frontally and passes over in the granular mass of the valvula. But in different Teleosts the two eminentiae granulares cannot be separated from the granular mass between them nor from the granular substance of the valvula. Moreover it is known also by the fiber connections, that the valvula cerebelli belongs to the acustico-lateral area.

In Ceratodus the granular mass of the eminentia extends as a tongue far frontally along the lateral side of the midbrain (fig. 1) HOLMGREN and VAN DER HORST have called this part the ganglion isthmi. It is not impossible, that this granular mass really is the ganglion isthmi, because also this ganglion is related to the acustico-lateral area. But it may also be possible, that this mass is the homologue of the valvula cerebelli which in this case should have extended along the lateral surface of the midbrain instead of curving into the ventricle of this brain part.

In Teleosts almost the same relations are found as in Amia; what was still in a rudimentary state in Amia, has developed farther in Teleosts. This concerns in particular the ventral molecular mass. Compared with Amia this mass extends by far more frontally and covers the whole ventricular side of the cerebellum. Also the place of attachment of the choroid plexus, covering the fourth ventricle, has shifted frontally, so that the caudal part of the cerebellum projects quite independently to the exterior.

In Osmerus the conditions are nearly the same as in Amia. Here also the cerebellum has the form of a thick curved plate (fig. 9). The ventral molecular mass extends here farther frontally (fig. 10), but still it disappears soon, when the cerebellum is attached to the dorso-lateral border of the oblongata. But in the more specialised Teleosts this ventral molecular layer extends below the whole corpus cerebelli. Moreover the cerebellum has increased in size considerably and it shows a different form in the different orders of Teleosts. It may grow high up as a solid mass, as is often the case in Acanthopterygii (fig. 11), or it remains more or less flat; it may be situated above the fourth ventricle as in Gadidae, or it may bend in frontal direction above the tectum opticum as in Siluridae.

Also the eminentia granularis varies greatly in development. This all has been described bij FRANZ for a great number of Teleosts.

I only will call attention here to the relation met with in Anguillidae (fig.

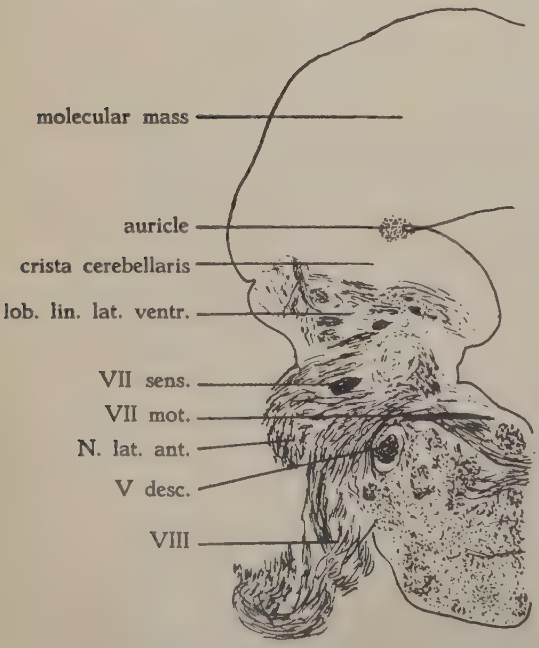

Fig. 9. Osmerus eperlanus.

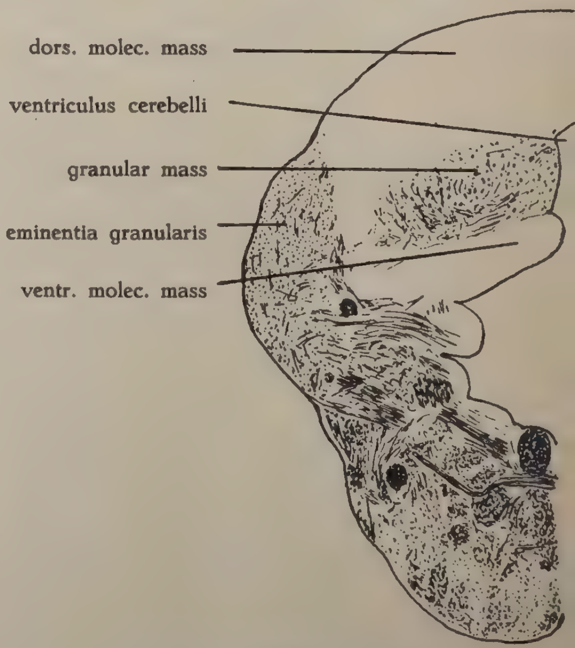

Fig. 10. Osmerus eperlanus.

12). Here the granular layer reaches the lateral surface along the whole length of the cerebellum. Also the granular mass consists clearly of two layers, the ventral one of which is in connection with the eminentiae granulares. These two layers are separated by a furrow on the lateral surface. According to FRANZ this is a primitive condition and it proves, that the cerebellum of Teleosts has developed from a plate-like state by curving upwards. This should correspond to a selachian cerebellum being so much flattened in fronto-caudal direction, that the ventricle should have quite disappeared. Only in some cases as in Anguilla, a limit between the dorsal and ventral granular layer should be visible.

In my opinion the cerebellum of Anguilla must be explained as follows: The eminentiae granulares are greatly developed and extend along the whole length of the cerebellum. Also the granular layer, which otherwise in Teleosts connects the two eminentiae only in the frontal part of the cerebellum, has enlarged in caudal direction. In this way two granular layers are visible externally over the total length of the cerebellum, the ventral one

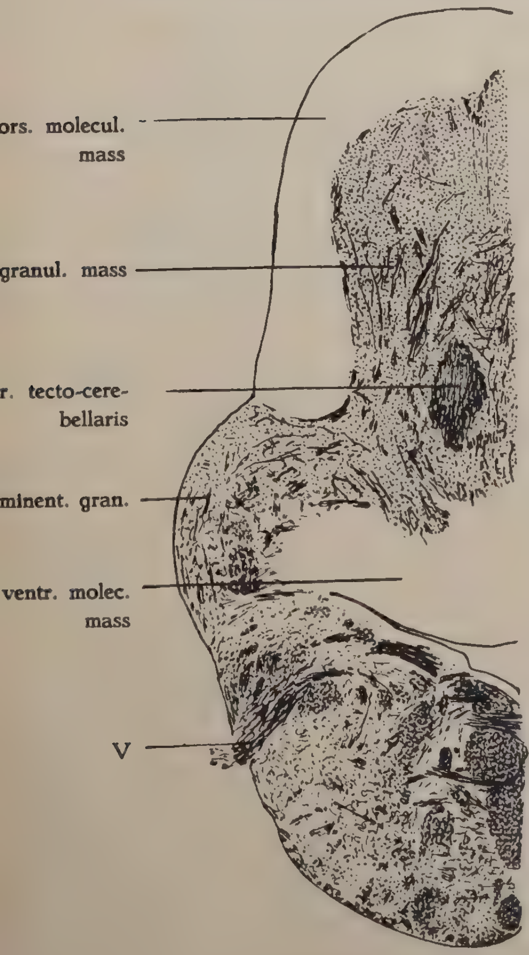

Fig. 11. Trachinus draco.

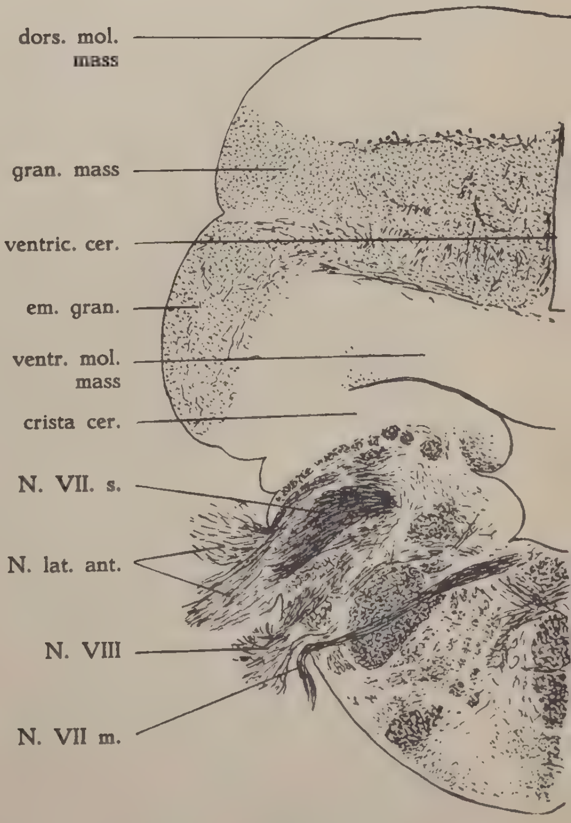

Fig. 12. Anguilla anguilla.

belongs to the eminentiae granulares, the dorsal one is the real granular substance of the corpus cerebelli. Also the latter granular substance reaches the surface in Anguillidae in contradistinction to the other Teleosts, and this may be in relation with the great depression of the cerebellum.

Finally I may show, that the ventriculus cerebelli in Amia and different primitive Teleosts, is not homologous to the ventriculus cerebelli in Selachians. In Teleosts this ventricle is a very narrow sagittal fissure, being a last remnant of the bilateral origin of the cerebellum as described by SCHAPER. If the opinion of FRANZ were correct, we might expect a horizontal or a transverse fissure instead of a sagittal one. The cerebellum of Selachians arises by folding upwards of a plate-like rudiment which is found in embryo's. So the ventriculus cerebelli in these animals is a part of the fourth ventricle separated from the rest by the folding upwards of the cerebellum. The only part of this ventricle which may be compared with the ventriculus cerebelli of Teleosts is the sagittal fissure between the two granular ridges.

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Chemistry. — *"On the Crystalstructure of Germanium-tetraiodide"*. By Prof. Dr. F. M. JAEGER, Dr. P. TERPSTRA and Mr. H. G. K. WESTENBRINK.

(Communicated at the meeting of September 26, 1926).

§ 1. In the following the results of the determination of the crystalstructure of *Germaniumtetraiodide*: GeI_4 are published, of which a small quantity was kindly presented to us by Prof. DENNIS [1]). At the same time a small quantity of the corresponding optically-uniaxial *Di-iodide*: GeI_2 was received, the crystals of which were, however, unsuitable for an investigation in its full extent. We hope, however, yet to be able within a short time to compare the structures of both these compounds in connection with the results of a study of some derivatives isomorphous with GeI_2.

In the first instance a number of diffraction-images were obtained after the method of HULL and DEBIJE, the source of radiation in this case being a copper-anticathode. The type of ROENTGEN-tube used was a dismantable gas-tube of cylindrical shape of the form used in Sir W. H. BRAGG's laboratory, and provided with an aluminium-window. The radiation used (at 50 K. V.; current: in mean 9 m.Amp.) consisted of copper-K-radiation of the wave-lengths: $\lambda_\alpha = 1{,}537$ A.U. and $\lambda_\beta = 1{,}388$ A.U., $\frac{\lambda_\alpha}{\lambda_\beta} = 1{,}107$. Occasionally a nickelfilter was made use of; however, afterwards this was dropped, because of the weakening of intensity, especially, as it appeared that the diffraction-images which belonged to each of these wave-lengths, could easily be discerned from each other. In these experiments the very finely powdered iodide was smeared upon a thin silk thread stretched along the axis of the cylindrical camera.

As an instance the values are given in the following table, measured by means of a comparator on one of the best films (N°. 18) obtained in this way; the radius of the camera was 24,76 m.M.

Evidently the line N°. 1 is the β-line corresponding to N°. 2; N°. 3 that corresponding to the β-line N°. 4; N°. 6 the β-line of N°. 7; N°. 8 that corresponding to the α-line N°. 9. Moreover, $\frac{\sin^2 \frac{\theta}{2}}{\Sigma(h^2)}$ is, for λ_α equal to: 0,00418 and for λ_β equal to: 0,00341; these numbers are, indeed, to each other in the proportion of $\left(\frac{\lambda_\alpha}{\lambda_\beta}\right)^2$. Although, if the two first values are not considered, the indices: (111), (200), (220), (311), (222), (331), (240) and (224) may be calculated directly from these measurements, it will become clear from the following determinations, that the line N⁰. 4 corresponds to the *second* order reflection on {111}. If the values N⁰. 1 and N⁰. 2 are also taken into account, it follows from these, that $\Sigma(h)^2$ for them is equal to 6, and the other forms observed will then obtain the values indicated in the table; evidently the images N⁰. 1 and 2 represent the first order images on {112}, line N⁰. 13 thus being the fourth order of them. In this connection it may be remarked also, that on Film N⁰. 12 a rather intense line was found for $\theta/_2 = 28°17'$, on Film N⁰. 7*a* one for $\theta/_2 = 25°16'$, corresponding to the third order reflections on {112} for λ_α en λ_β; the theoretical angles are here: 28°22′, resp.: 25°24′. On the contrary. the corresponding images of the second order were nowhere observed with certainty.

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[1]) L. M. DENNIS, Journ. Amer. Chem. Soc., **44**, 2856, (1922).

Analysis of Film N⁰. 18.

Number of the lines from the centre	Distance l of the images on both sides in m.m.	Wave-length	Estimated intensity	2θ	$\theta/_2$	sin $\theta/_2$	sin² $\theta/_2$	Indices
1	$l/_2$ = 7.17	λ_β	extremely weak	θ=16°36′	8° 18′	0.1444	0.0208	(112)
2	$l/_2$ = 7.88	λ_α	very weak	θ=18 14	9 7	0.1584	0.0251	(112)
3	20.29	λ_β	5	47 16	11 44	0.203	0.0412	(222)
4	22.49	λ_α	10	52 4	13 1	0.225	0.0506	(222)
5	26.00	λ_α	7	60 12	15 3	0.260	0.0676	(400)
6	33.31	λ_β	3	77 8	19 17	0.333	0.1089	(440)
7	37.11	λ_α	9	85 56	21 29	0.366	0.1340	(440)
8	39.33	λ_β	1	91 4	22 46	0.387	0.1497	(622)
9	43.85	λ_α	8	101 32	25 23	0.429	0.1840	(622)
10	$l/_2$ = 22.97	λ_α	3	106 20	26 35	0.448	0.2007	(444)
11	59.18	λ_α	3	137 0	34 15	0.563	0.3169	(662)
12	60.92	λ_α	3	141 4	35 16	0.577	0.3329	(480)
13	67.64	λ_α	2	156 36	39 9	0.631	0.3981	(448)

From these measurements it can be deduced, that here a cubic space-lattice is present in the structure: from $\frac{\lambda_\alpha^2}{4a^2} = 0{,}00418$ and $\frac{\lambda_\beta^2}{4a^2} = 0{,}00341$, the edge a of the elementary cubic cell is calculated:

$$a = 11{,}89 \text{ A.E.}$$

As the volume V of this cell is 1679 cubic A.U. $= 1679.10^{-24}$ ccm., and as DENNIS 1) determined the specific weight d of the crystals (in sulphuric acid) at 26° C. on: 4,3215, the number N of the molecules GeJ_4 ($M = 580{,}18$) in this cell is calculated as: $N = \frac{V \, . \, d}{M \, . \, 1{,}64.10^{-24}} = 7{,}63$; evidently, therefore, the cell contains 8 molecules GeJ_4, and the true specific weight 2) of the crystals must be: $d_{4^\circ} = 4{,}534$.

Besides the films mentioned here, also some photographs were prepared after HULL's method on flat films; although very faint, also in this case the lines of $\{112\}$ were observed here. One of these radiograms proved, moreover, without any doubt, that the line N⁰. 3 is indeed no other than the line for λ_β, corresponding to N⁰. 4.

Film N⁰. 18 was tested, moreover, by the aid of a photometer-arrangement with a thermoelectrical cell and mirror-galvanometer with respect to its differences in intensity. In fig. 1 the results of these measurements on one half of the film are plotted graphically. Besides the images already mentioned above, the presence of the images of the first order (for α- and β-radiation): $\{111\}$, $\{221\}$, $\{421\}$, $\{411\}$, $\{432\}$, $\{731\}$, etc., although comparatively weak, was revealed, as well as that of those of $\{112\}$.

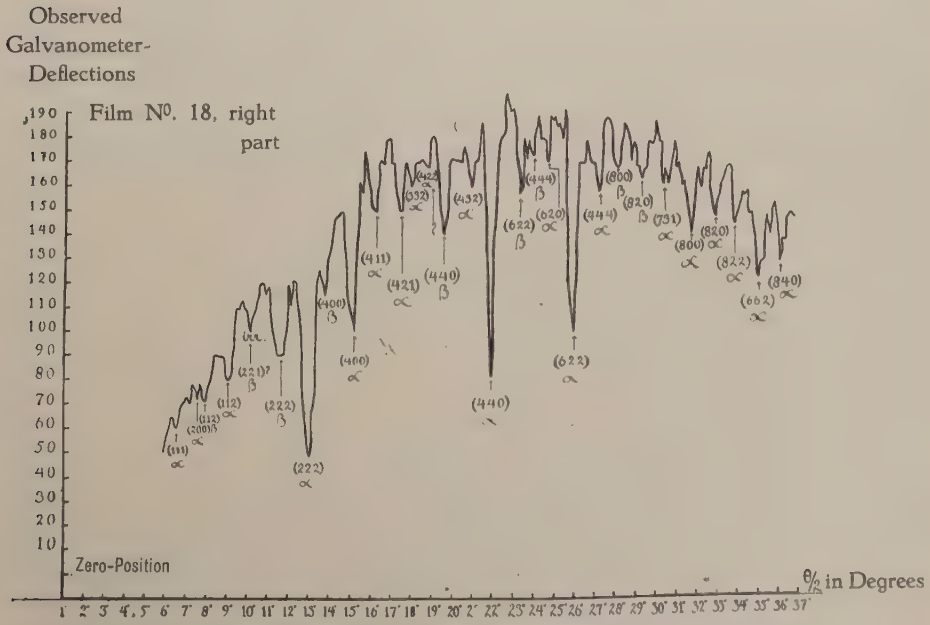

Fig. 1. *Photometrical curve of Film N⁰. 18.*

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1) Loc. cit., p. 2856. As GeJ_4 in contact with solvents is extremely easily decomposed, so it is probable, that in reality no solvents will be without action upon this substance, — the deviations in d thus being explicable.

2) From the measurements on the other films a value for a is deduced, not appreciably deviating from 12 A.U. In this case, d_{4° would be: 4,405.

Because of the general veil superimposed upon all these lines, it is, however, impossible to determine the absolute intensity of these lines. The most intense lines correspond to {111}, {331} and {311} in the *second* order; to {100}, {110} and {210} in the *fourth* order; to {100} in the *eighth* order etc.

Further confirmation of this was again obtained by means of a rotation-radiogram, a perpendicular to the edge of one of the triangular octahedron planes being chosen here as vertical axis of revolution. Besides some other images, those of {222}, {444}, {622}, {440} and {662} appeared to be present upon it; but there was, for instance, no indication of {100} or {110}.

§ 2. For the purpose to obtain full certainty about the orders of the diffraction images mentioned above, measurements were made on a plate parallel to {111}, after BRAGG's spectrographic method. The crystalplates parallel to {111} were obtained by slow evaporation of a solution of the iodide in carbondisulphide in a vacuum. The very thin triangular plates thus obtained were mounted carefully on thin glass-plates, put upon the X ray spectrometer and given a slow oscillating motion along the axis of the instrument by means of a clock-work. To determine accurately the distance between the crystal-plate and the central spot on the photographic plate, two photograms were made on the same film, this being placed in parallel positions at two different distances a_1 and a_2. The shift $a_2 - a_1 = w$ was measured very accurately; by measuring also on the film the distances s_1 and s_2 of two corresponding lines, e.g. that of the lines for λ_α of λ_β, in both cases, the distance x, where the plate stood in the first experiment, can be easily calculated; for: $\frac{x}{x+w} = \frac{s_1}{s_2}$. If θ is the glancing angle, at which the diffraction takes place, then evidently $tg\ 2\theta = \frac{s_1}{2x}$, so that, θ being now determined, the spacing $d_{(111)}$ of the reticular planes may be calculated from the formula: $2d_{(111)} . \sin\theta = n . \lambda$.

In this way for $x = 45{,}82$ mm. and for $\lambda_\alpha = 1{,}54$ A.U. [1]), s_1 was found to be: 44,10 mm.; therefore, $\theta_\alpha = 12°51'$; in the same way, for $\lambda_\beta = 1{,}389$ A.U. and $x = 45{,}40$ mm., s_1 was found to be: 39,09 mm., θ_β thus being: 11°39'. If these spectra be *second* order spectra, $d_{(111)}$ becomes: 6,924 A.U., resp.: 6,879 A.U., in mean: 6,901 A.U. Indeed, if in a cubic space-lattice the edge a be really equal to 11,9 A.U., $d_{(111)} = \frac{1}{3} a \sqrt{3}$ must be: 6,90 A.U. The intensive image N⁰. 4 film 18 thus corresponds really to (222). The spectrum of the fourth order must, therefore, be situated at a distance from the central spot (for λ_α), equal to: 60.34 mm., when x again is 45.82 mm. ($2\theta = 52°48'$). With an exposure during 10 minutes (8 to 10 milli-Amp.), this image was really found at its right place on the films X and X', and that very intensive. For the spectrum of the first order, the distance to the central spot for λ_α should be: 10.38 mm. and for λ_β: 9.31 mm. Indeed, both these spectra could be stated, be it extremely faint, on film III; their intensities are incomparably fainter than those of the second and fourth order [1]. Even if (on film III) the spectrum of the first order was exposed during 37 minutes, that of the second order during only 5 minutes, the intensity of the first image appeared to be very much smaller than that of the last image.

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[1]) Actually in the K radiation of copper: $\lambda_{\alpha_1} = 1{,}537$ A.U. and $\lambda_{\alpha_2} = 1{,}543$ A.U.; on an average therefore $\lambda_\alpha = 1{,}540$ A.U. For λ_β the value: 1,389 A.U. was used; β is here equivalent to β_2 in the table above.

Finally these experiments were executed once more with a silver-anticathode, which gives a radiation of $\lambda = 0.565$ A.U. Now the spectrum of the second order appeared at: $2\theta = 9°24'$; the distance of both images to the central spot now being: 7.52 mm., with $x = 45.5$ mm. ($s_1 = 15.1$ mm.); in the same way the spectrum of the fourth order appeared at a distance from the central spot of: 15.52 mm. ($s_1 = 31.4$ mm.) and with an appreciable intensity ($2\theta = 18°50'$). The spectrum of the third order must be found at: $2\theta = 39°6'$, i. e. at a distance from the central spot of: 36.97 mm., if copper-radiation of λ 1.540 A.U. be used; its distance from the *second* order spectrum (see above) therefore being: $36.97 - 22.05 = 14.9$ mm. The experiment was made in such a way, that the spectrum of the second order was exposed only 5 minutes, but that of the third order 30 minutes (film VI), and notwithstanding this, an extremely faint image appeared to be hardly visible in the calculated place.

By all these experiments it is convincingly proved, that on (111) diffraction occurs in such a way, that the spectra of the first and third order are extremely faint, those of the second and fourth order, however, very intensive.

§ 3. In trying to solve the problem: to which of the 230 space-groups do the crystals of GeI_4 really belong?, — it is necessary also to keep in mind, that the specific diffracting influence of the *I*-atoms, which are four times as numerous, is very different from that of the *Ge*-atoms, and also, that the absorption of ROENTGEN-rays is very different for both [2].

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[1] During the preparation of film III the aluminum window of the tube appeared to be gradually covered with volatilized copper. Because of the unequal absorption thus taking place, the lines corresponding to λ_β appeared now to be more intensive than those for λ_α.

[2] The strong absorptive power of iodine in this salt, manifested itself also in preparing the radiograms after VON LAUE: it was only possible to get them, if extremely thin plates were made use of.

A first step towards this solution of the problem was the determination of the crystallographical symmetry. With some small crystals obtained from a solution in benzene, a number of very small facets were observed at the corners of one of the planes of the octahedron. The crystal was measured by means of a goniometer with two circular divisions; the plane (112) being taken as polar facet. The following reflexes were localised:

Face	φ	ρ	Kind of reflection:	Index of Crystal-plane
χ	0°	19° 38′	sharp	(111)
β	129	23 57	very sharp	(102)
γ	0	90 10	sharp	$(11\bar{1})$
δ	34	34	faint	(211)
ε	25	57	very faint	(210)
ζ	184	69	very faint	$(\bar{1}\bar{1}2)$
η	204	56 35	sharp	$(\bar{1}02)$
ϑ	209	27	very faint	?
ι	$294^1/_4$	42 37	sharp	(021)
$\varkappa$	330	35	very faint	(121)
λ	34	32	faint	(211)
μ	124	37	faint	?
ν	114	62 15	sharp	$(1\bar{1}1)$
o	182	34 59	very sharp	(001)
σ	313	65	very faint	(010)
τ	34	31	very faint	(211)
τ, μ and δ are parts of the same facet; φ = (112)				

A stereographic projection of the forms observed is reproduced in Fig. 2. Evidently is a combination present of an *octahedron* {111}, a *hexahedron* {100}, an *icositetrahedron* {211} and a *pentagonaldodecahedron* {210}; the zonal relations in the projection-figure make this sufficiently clear.

The symmetry of the crystals can, therefore, only be that of the *tetrahedral-pentagonaldodecahedral* class ($3\Lambda_2$; $4L_3$; $0L_2$; $0\Pi_4$; $0P$; $0C$), or that of the *dyacisdodecahedral* class ($3\Lambda_2$; $4L_3$ $(=\bar{L}_6)$; $0L_2$); $3\Pi_2$; $0P$; C).

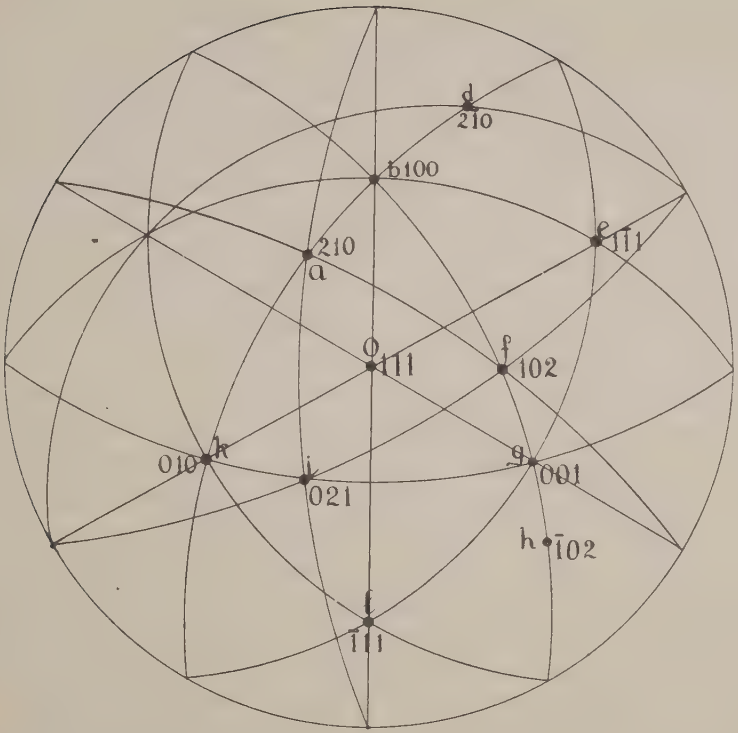

Fig. 2. *Stereographical Projection of the observed Forms on a plane of* {111}.

§ 4. It is *a priori* excluded to make a final choice between these two classes of symmetry by means of a LAUE-photograph of a crystal-plate cut parallel to (111); other plates were, moreover, not at our disposition. For, as one of us [1]), in collaboration with H. HAGA, was able to prove formerly, such LAUE-radiograms must always show the same symmetry as a similarly orientated plate of a crystal, whose symmetry is that of the crystal under investigation after a centre of symmetry has been added to it. But as in both classes mentioned *no* axes of twofold symmetry perpendicular to the faces of the rhombododecahedron do occur, these faces can *never* appear as planes of symmetry in the LAUE-radiogram on (111), if a centre of symmetry is thought to be added to the tetrahedral-pentagonaldodecahedral symmetry, nor will this be the case with a dyacisdodecahedral crystal, because this does already possess such a centre of symmetry. The LAUE-radiogram obtained by radiation perpendicular through a plane of (111) can, therefore, in both cases only show an axis of threefold symmetry, *without* any symmetrical arrangement of its spots with respect to three planes intersecting along this axis under 120° (60°). Notwithstanding this fact, such a LAUE-radiogram was yet prepared, because it seemed of interest for the further determination of the crystalstructure. A very thin plate parallel to (111) was for this purpose stuck to a thin glass-plate and a diffraction-image made in the usual manner by means of a MÜLLER-gas-tube with a platinum-anticathode and an osmotic pressure-regulation (60 K. V.). The glass-plate was orientated as accurately as possible by means of a goniometer-arrangement; the time of exposition was 5 hours (with 4 milli-Amp.). The image appeared, however, yet to be not completely symmetrical, as a consequence of a slight deviation in the direction of the *X*-rays from the normal on (111); notwithstanding this, however, it could be clearly shown, that the LAUE-radiogram was undoubtedly symmetrically built with respect to three diameters intersecting at 120° (60°). The cause of this abnormal behaviour must doubtlessly be attributed to the great differences in diffracting power, already mentioned, of the numerous iodine-atoms on the one hand, in comparison with that of the germaniums-atoms on the other hand, which are four times as scanty, in connection with a particular kind of mass-distribution of both atomic species throughout the structure as a whole. Here, indeed, is found a

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[1]) H. HAGA and F. M. JAEGER, These Proceedings **17**, **18**, **19**.

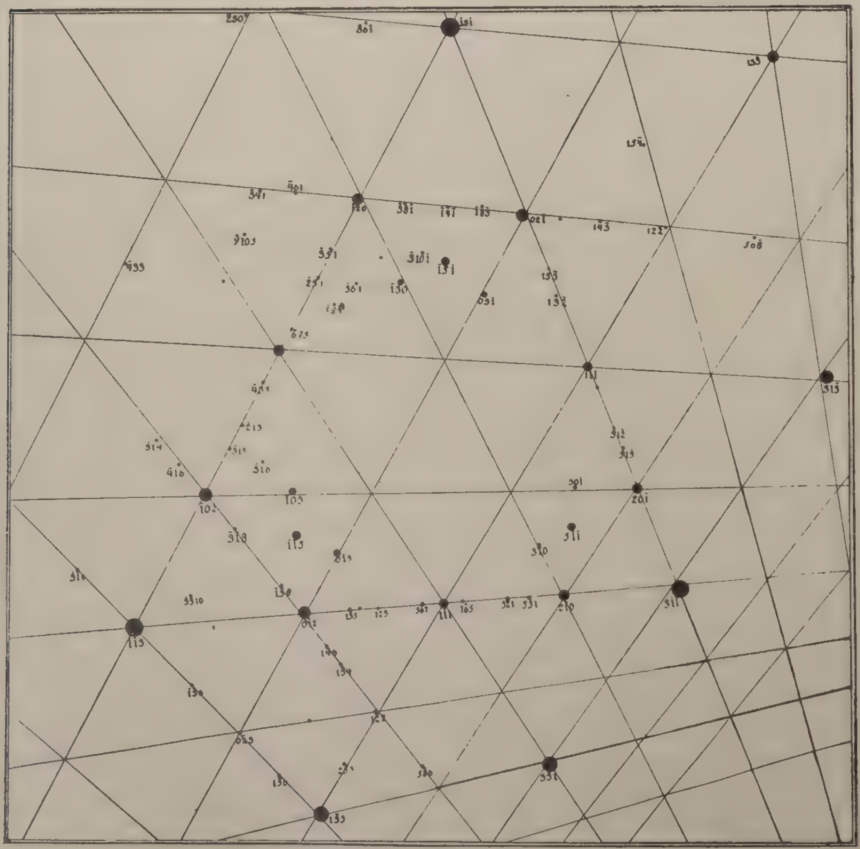

Fig. 3. *Gnomonic Projection of the* LAUE*-radiogram on* $\{111\}$.

new instance of the already known phenomenon, that the symmetry of such LAUE-radiograms can occasionally be deceptive in so far, as symmetry-elements may be apparently present, which are incompatible with the proper crystallographical symmetry, but only manifest themselves as a consequence of accidental peculiarities of the atomic arrangement.

A gnomonic projection of this LAUE-radiogram is reproduced in Fig. 3. The distance l of the spots from the central one and that ($s = 4$ c.m.) of the film and the crystal-plate being known, — the indices of the diffracting planes and the sinus of the angles θ could be calculated from the relation: $l = s \, . \, tg \, 2\theta$; at the same time the intensities of these spots were approximately estimated. As the edge a of the cubic cell (= 11,89 A.U.) is known, the distances d between the diffracting planes (hkl) can be directly calculated [1]) in A.U. and by these values for d it is possible to determine the product $n \, . \, \lambda$ in the formula: $2 \, d \, . \, sin \, \theta = n\lambda$ or in $\frac{2a \, . \, sin \, \theta}{\sqrt{h^2 + k^2 + l^2}} = n \, \lambda$. Now the voltage of the gas-tube in these experiments was 60 K.V.; the maximal intensity of the polychromatic platinum-radiation, therefore, must be situated in the neighbourhood of 0,4 or 0,5 A.U. [2]) On this supposition it appears possible, by comparison of the relative intensities, to estimate with a high degree of probability the values of n, i. e. of the *orders* of the observed spots: inversely, the sequence of the intensities [3]) for each value of λ thus calculated, gives a control with respect to the right choice of the multiplicators n. In this way the data could be obtained, which are collected in the table on page 756.

If the estimated intensities are graphically plotted against the deduced wave-lengths [4]), a graph is obtained as reproduced in Fig. 4. The sequence of the observed, relative intensities for the faces of the same form $\{hkl\}$ appears really to be just the same, as might be expected in connection with the shape of the curve for the energy-distribution in the ROENTGEN-spectrum, if a voltage of 60 K.V. be applied to the tube.

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[1]) R. W. G. WYCKOFF, *The Structure of Crystals*, (1924), p. 452; P. P. EWALD, Ann. der Physik. **44**, (1914), p. 257. Also here θ is equivalent to $\theta/2$ in the above.

[2]) In WYCKOFF's book is given a graph of the intensity-distribution for the different wave-lengths λ of the *tungstene*-spectrum, as shown on the photographic plate, if a voltage of 60 K.V. is applied. The intensity increases from the shorter wave-lengths rapidly until a maximum at about 0,484 A.E., this being the characteristic limit of absorption for *silver*. As *platinum* in the periodic table is close to *wolframium*, the energy-distribution in the platinum-spectrum under 60 K.V. will *grosso modo* show great analogy with that of the other metal. It is this supposition, which is made use of in the determination of the numbers n of the spots considered.

[3]) It need hardly to be said again, that the estimations of the relative intensities (10 for the most intensive, 1 for the faintest spots) can have no other significance than as rough indications of the existing differences. The numbers attributed to the spots only will express, that one spot is darker than another.

[4]) R. W. G. WYCKOFF, Amer. Journal of Science, **50**, (1920), 318, P. P. EWALD, *Krystalle und Roentgenstrahlen*, p. 115.

Table of Diffraction-spots in the LAUE-radiogram

Distance of the Spot from the centre in m.M.:	Index of the diffracting planes:	*sin θ*	n. λ in A.U.	Orders n:	λ in A.U.	Estimated intensity:
32.5	$(11\bar{1})$	0.335	4.65	8	0.58	5
26.0	$(\bar{1}11)$	0.284	3.94	8	0.49	6
34.5	$(1\bar{1}\bar{1})$	0.348	4.83	8	0.60	4—5
25.2	$(20\bar{1})$	0.278	2.98	4	0.74	5—6
22.5	$(0\bar{1}2)$	0.253	2.71	4	0.68	6—7
18.0	$(\bar{1}20)$	0.210	2.25	4	0.56	6 (+)
26.0	(210)	0.284	3.04	4	0.76	5—6
20.0	$(\bar{1}02)$	0.230	2.47	4	0.62	7 (—)
20.0	(021)	0.230	2.47	4	0.62	6—7
27.8	$(\bar{1}5\bar{1})$	0.300	1.40	2	0.70	4—5
36.0	$(5\bar{1}\bar{1})$	0.359	1.66	2	0.83	4 (—)
29.0	$(\bar{1}1\bar{5})$	0.310	1.43	2	0.71	5 (—)
13.3	$(\bar{1}\bar{1}3)$	0.158	1.14	2	0.57	10
17.5	$(3\bar{1}\bar{1})$	0.206	1.50	2	0.75	8
11.0	$(13\bar{1})$	0.134	0.97	2	0.49	10
40.0	$(30\bar{1})$	0.383	2.91	4	0.73	2
35.1	$(0\bar{1}3)$	0.353	2.68	4	0.67	3—4
30.4	$(\bar{1}30)$	0.320	2.43	4	0.61	3
41.5	$(3\bar{1}0)$	0.391	2.96	4	0.74	2
32.4	$(\bar{1}03)$	0.335	2.55	4	0.64	3—4
33.5	$(03\bar{1})$	0.342	2.59	4	0.65	3
15.2	$(5\bar{8}6)$	0.181	0.39	1	0.39	1
13.2	(568)	0.158	0.34	1	0.34	1 (—)
9.8	$(13\bar{3})$	0.120	0.66	2	0.33	6
12.0	$(1\bar{3}3)$	0.145	0.80	2	0.40	8 (—)
13.6	$(3\bar{3}1)$	0.162	0.89	2	0.45	8
12.0	$(31\bar{3})$	0.145	0.80	2	0.40	7—8

This result may serve as an argument for the correctness of the calculated values of λ for each sport, and consequently for those of the numbers n. All the sections of curves in this graph are evidently parts of intensity-curves showing a maximum in the vicinity of 0.5 A.U. In connection with this, it may be, moreover, remembered, that in the DEBIJE-films the image of {201} has indeed but an appreciable intensity in the *fourth* order; also {331} appears in it only in the *second* order with a measurable intensity. By the BRAGG-method it was found, that {111} only shows a considerable intensity for *even* orders, while {113} has the greatest intensity as well in the DEBIJE- as in the LAUE-radiogram, etc. Moreover, the results obtained in the rotation-radiogram mentioned before, are also in best concordance with all this.

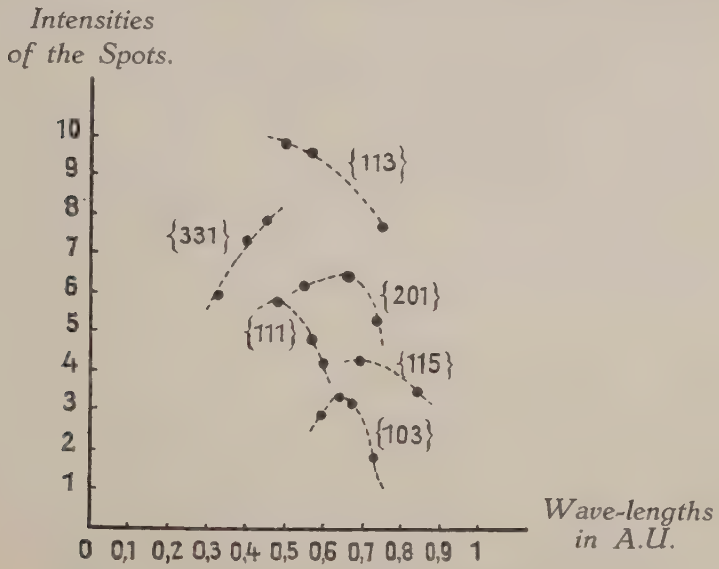

Fig. 4. *Distribution of Intensities in the* LAUE-*radiogram.*

§ 5. If now it be considered that in the powder-radiograms a faint image of {111} and of {112} of the first order was found, as well, although very faint, of {221}, {441} and {432}, while it appears now from the discussion just given, that among the spots of the LAUE-image there is present also a first order image of {586}, — then it must be clear, that images of the *first* order are possible in this structure of planes having *three* odd, *two* odd, or *two* even indices. This fact, — combined with the evidence brought in the foregoing pages, that the spectra on {111} are very intensive in the second and fourth, but very faint in the first and third order, — enables us with a high degree of probability to make our choice between the twelve space-groups, which only are compatible with the two symmetries possible in this case.

If the three fundamental translation-groups (BRAVAIS' space-lattices) of the space-groups considered are discerned as follows: Γ_c for the simple cubic, Γ_c'' for the body-centred, and Γ' for the face-centred cubic space-lattice, — then the twelve space-groups here only of interest, can be tabulated as follows [1]):

Symbol of the Space-groups of dyacisdodecahedral and of tetrahedral-pentagonal-dodecahedral symmetry	Corresponding translation-group :	Number of points equivalent to each point of the Space-group :
T_1	Γ_c	12
T_2	Γ_c'	48
T_3	Γ_c''	24
T_4	Γ_c	12
T_5	Γ_c''	24
T_h^1	Γ_c	24
T_h^2	Γ_c	24
T_h^3	Γ_c'	96
T_h^4	Γ_c'	96
T_h^5	Γ_c''	48
T_h^6	Γ_c	24
T_h^7	Γ_c''	48

In the last column the number of equivalent points is indicated, corresponding to each arbitrarily chosen point of the group. If through each of these corresponding equivalents molecular planes be passed parallel to each other, their sequence will appear to be such, that the diffraction-images of definite orders must be cut out by interference. It can be foreseen [2]), that:

a. if the fundamental translation-group is Γ_c, there will appear diffraction-images of *all three* kinds of planes $\{hkl\}$ in *all* orders;

b. if the translation-group is Γ_c', there will appear in *odd* orders only images of planes $\{hkl\}$ with *three odd indices*;

c. if the translation-group is Γ_c'', there will appear in *odd* orders only images of planes $\{hkl\}$ with *two even* indices and one *odd* index; in all these cases *zero* being considered as *even* index.

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[1]) R. W. G. WYCKOFF, *The analytical Expression of the Results of the Theory of Space-groups*, p. 33 and 34.

[2]) R. W. G. WYCKOFF, loc. cit., IV, (1922), p. 175, 181, 183; W. T. ASTBURY and K. YARDLEY, Phil. Trans. R. Soc. London, A **224**, (1924), p. 222.

With respect to the facts mentioned above, it must be clear now, that, as among the images of *odd* order such appear not only of $\{111\}$ and $\{731\}$, but also of $\{221\}$, $\{421\}$, $\{432\}$, $\{568\}$, and of $\{112\}$ and $\{411\}$, the fundamental translation-group can only be Γ_c, i. e. the *simple cubic space-lattice*. For Γ_c'' is excluded by the first order of $\{111\}$ and Γ_c' by that of $\{112\}$, while the presence of the first order spectrum of $\{568\}$ is in full agreement with the presence of Γ_c. Of the twelve space-groups mentioned, thus only *five*: T^1, T^4, T_h^1, T_h^2, and T_h^6 need to be further considered here.

For each of these five groups is the relation of the consecutive values of $sin^2 \dfrac{\vartheta}{2}$ as follows [1]:

For T_1 and T_h^1:	1 : (100)	2 : (110)	3 : (111)	4 : (200)	5 : (201)	6 : (211)	8 : (220)	9 : etc. (221)	
For T_4:		2 : (110)	3 : 111)	4 : (200)	5 : (201)	6 : (211)	8 : (220)	9 : (221)	10 : etc. (301)
For T_h^2:		2 : (110)	3 : (111)	4 : (200)		6 : (211)	8 : (220)	9 : etc. (221)	
For T_h^6:			3 : (111)	4 : (200)	5 : (102)	6 : (211)	8 : (220)	9 : etc. (221)	

In the row of observed diffraction-images there are certainly absent those of the first order on (100) and (110); for this reason the four groups: T^1, T_h^1, T^4 and T_h^2 are excluded, — thus only T_h^6 remaining. For this group is true, that images of planes $\{h0l\}$, in which h is *even* and l is *odd*, or those of $\{0kl\}$, in which k and l are both *odd*, can*not* appear in *odd* orders [2]). Indeed, among the observed images, that of $\{201\}$ is *not* present; in the LAUE-radiogram the *fourth* order spectra of $\{201\}$ and $\{102\}$ have about the same intensity, which indicates that the diffracting power of both these planes is about identical and explains also the absence of the first order of $\{102\}$, so that this absence needs not to be considered an argument against T_h^6 in this case. In favour of T_h^6, on the other hand, it may be remembered, that besides the first order spectra on $\{100\}$ and $\{110\}$, also that of $\{031\}$ is absent, — which follows from the powder-radiogram, where the row of consecutive $sin^2 \dfrac{\theta}{2}$ was:

$$3 : 6 : 8 : 16 : 22 : 24 : 38 : 40 : 48;$$

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[1]) Or of: $(h^2 + k^2 + l^2)$. Cf. i.a. P. NIGGLI, Zeits. f. Kryst. **57**, (1922), 261; *idem, Geometrische Kryst. des Diskontinuums*, Table X, p. 482.

[2]) R. W. G. WYCKOFF, loc. cit., p. 183.

i.e. possesses even more scanty terms, as is postulated with respect to what has been said above.

It is now necessary to fit 8 molecules GeI_4 into the fundamental cell with its edges of 11,89 A.V., i.e. 8 *Ge*-atoms and 32 *J*-atoms. With respect to their *structural* function, these 32 *J*-atoms, although chemically equivalent, need *not* be all in the same condition: in general, the possible cases would be either that they have all (32) the same structural function, or that such is the case with 16 on the one hand and 16 on the other; moreover, it is possible to discern 16 atoms of one kind, 8 of a second kind and 8 of a third function in spatial respects; or to have 24 atoms of one and 8 of a second kind; or finally, there would be possible four groups of 8 atoms, each group differing from the others by its spatial relation in the space-group considered. But, as is seen from the table on page 758, the number of equivalent points in each of the five here possible space-groups can be no other than 12 or 24; in *no* case will it be possible, therefore, that the 32 *J*-atoms will have identical functions 1) in the structure of GeI_4, and neither will it be possible that 16 atoms of one and 16 atoms of a second kind are present in this structure. Moreover, groups of 8 equivalent atoms cannot be present in the space-groups T_1 and T_4 ($n = 12$); in T_h^1, T_h^2 and T_h^6 an arbitrary number of 8 equivalent atoms of one kind and 24 of another kind may be present, but no group of 16 atoms. From this also follows, that T^1 and T^4 are excluded. T_h^1 also is highly improbable, because in this case *no* $sin^{2\theta}/_2$ will be excluded from the series of values observed, while, as was shown, the number of missing values in this row appeared to be rather great in the powder-radiograms obtained. As the fundamental translation-group now is certainly Γ_c, and not Γ_c', the 32 *J*-atoms cannot be present in the structure in any other way than as: $24 + 8$. Regarding all these arguments, there can, in every case, only be a choice between T_h^2 and T_h^6; and this choice can be fixed only by consideration of the lack of certain diffraction-images of odd order.

The forms $\{103\}$ and $\{301\}$ for instance, can in T_h^2 give spectra as well in the even, as in odd orders; in T_h^6, however, only in even orders. On no radiograms, indeed, occur images of these forms in the first or in the third order; but those of $\{602\}$ and $\{12.04\}$ are present. (Film XII). On the LAUE-radiograms also $\{12.04\}$ is present. This is in contradiction with T_h^2, but in agreement with T_h^6. In the same way $\{330\}$ is everywhere absent; but $\{440\}$ and $\{880\}$ are all observed together on the powder-radiograms. These facts also lead to the same conclusion with respect to the two space-groups considered here.

In T_h^2 the reflections on $\{201\}$ and $\{102\}$ may only occur in even orders, in T_h^6 however, those on $\{201\}$ only in even, but those of $\{102\}$ as well in even as in odd orders, as was already emphasized. The fact,

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1) R. W. G. WYCKOFF, *The analytical Expression,* etc., p. 176.

that neither on $\{201\}$, nor on $\{102\}$ diffraction-images of odd orders are met with on the different photograms, need *not* be considered here as an argument against T_h^6, if the LAUE-radiogram be also taken in account. Summarizing all evidences, we think it highly probable, that GeI_4 has a structure[1]) corresponding to T_6^h.

§ 6. The most simple supposition with respect to the arrangement of the eight GeI_4-molecules, which can be made in concordance with all data acquired, leads to the structure reproduced in Fig. 5.

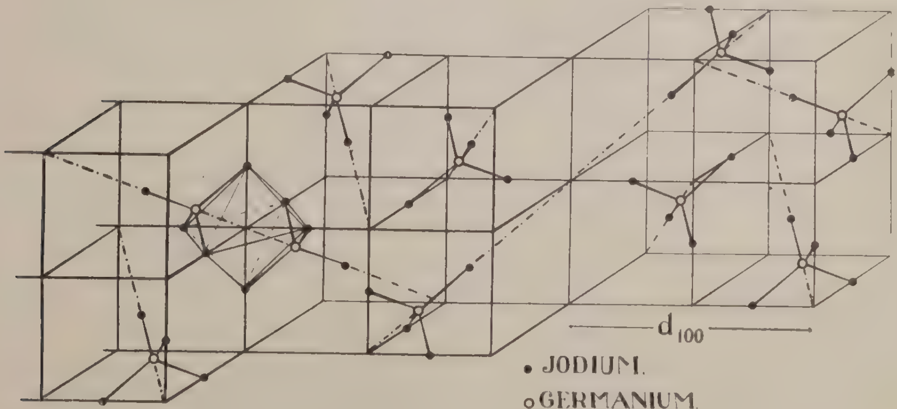

Fig. 5. *The Crystal-structure of Germaniumtetraiodide.*

Each *Ge*-atom in it appears as surrounded by four *J*-atoms, situated in the corners of a regular tetrahedron; from this it may be easily proved, that of the 32 *J*-atoms in each cell really 24 have equivalent positions in the structure and 8 a somewhat other structural function. For two GeJ_4-groups on each cube-diagonal of the fundamental cell can every time be thought to be combined in pairs, situated at equal distances of the centre to both sides of it; in such pairs evidently 6 *J*-atoms are always in equivalent positions with respect to each other, while 2 others have a somewhat different position, being directed more to the outsides of the combination. The *J*-atoms of such a pair are placed in the corners of a steep rhombohedron, the axis of which is a diagonal of the cubic cell; the nearest *Ge*-atoms, however, are then situated in the corners of an obtuse rhombohedron, coaxial with that of the *J*-atoms. In the combined pair of molecules both the *Ge*-atoms are placed in the centra of two diametrically opposed tetrahedra, the corners of which are occupied by the *J*-atoms. In the direction of a cube-diagonal planes of *J*-atoms alternate with such as are occupied by *Ge*-atoms in the way indicated in Fig. 6. Of course, this placing of the GeI_4-molecules is somewhat arbitrary, because the *J*-atoms may be thought shifted more or less along the cube-diagonal; in this case again 5 variable parameters must be determined by comparison of observed and calculated intensities of the diffraction-images, — a task, which may safely be considered to be impractable. In how far the here adopted structure can be considered to be in agreement with the observed relative intensities of the diffraction-images for the different planes on the DEBIJE-radiograms, may be seen from the data in the following table, in which the results are reviewed of the calculated values for a number of important crystal-planes.

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[1]) R. W. G. WYCKOFF, *The analytical Expression of the Results of the Theory of Space-Groups*, p. 127; P. NIGGLI, *Geom. Kryst. des Diskontinuums*, p. 367.

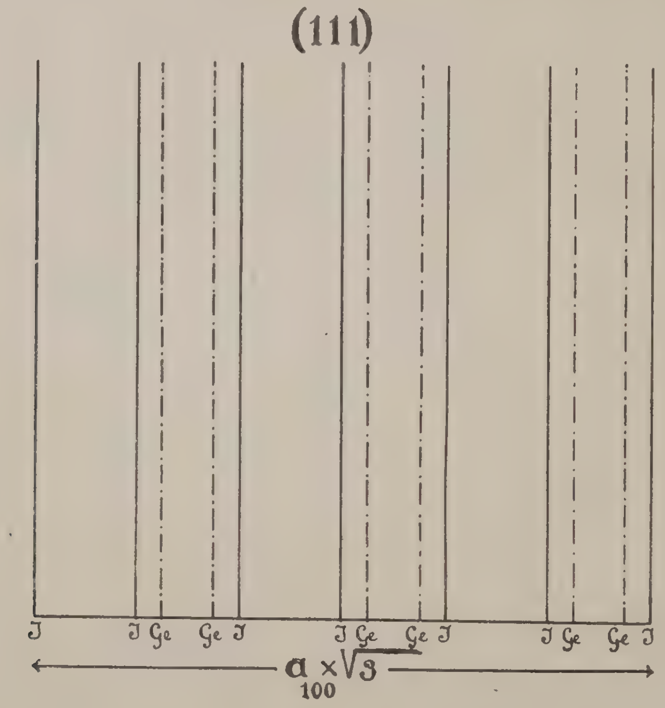

Fig. 6. *Successive molecular Planes along a Perpendicular to* {111}.

If in the formula for the intensities:

$$I = \frac{1+\cos^2\theta}{2\cos{}^{\theta}/_{2} \cdot \sin^2{}^{\theta}/_{2}} \cdot n \cdot |S|^2,$$

in which n is the number of planes of the crystal form $\{hkl\}$ and $|S|$ is the absolute value of the structural factor, the function preceding $n \cdot |S|^2$ be called: $f({}^{\theta}/_{2})$, then the value of this function for different forms $\{hkl\}$ and for successive orders, may be immediately read from the existing tables [1]). Moreover, for *Ge* and *I* in the formula for $|S|$

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[1]) L. WEBER, Zeitschr. f. Kryst. **57**, 402, (1923).

are taken the atomic numbers 32 and 53 respectively[1]) while the coordinates of the 24 + 8 *J*-atoms and of the 8 *Ge*-atoms are the following:

I. 32 *J-atoms;* x, y, z and v-along the cube-edges.

a. the 24 equivalent atoms:

0	0	1/4	1/2	1/2	—1/4	0	1/2	1/4	1/2	0	3/4
1/4	0	0	—1/4	1/2	1/2	1/4	0	1/2	3/4	1/2	0
0	1/4	0	1/2	—1/4	1/2	1/2	1/4	0	0	3/4	1/2
0	0	—1/4	1/2	1/2	1/4	0	1/2	3/4	1/2	0	1/4
—1/4	0	0	1/4	1/2	1/2	3/4	0	1/2	1/4	1/2	0
0	—1/4	0	1/2	1/4	1/2	1/2	3/4	0	0	1/4	1/2

b. the 8 equivalent atoms; $v = 1/4$.

1/4	1/4	1/4	3/4	1/4	—1/4	—1/4	3/4	1/4	1/4	—1/4	3/4
—1/4	—1/4	—1/4	1/4	3/4	1/4	1/4	1/4	3/4	3/4	1/4	1/4

II. 8 *Ge-atoms;* $v = 1/8$.

1/8	1/8	1/8	5/8	3/8	—1/8	—1/8	5/8	3/8	3/8	—1/8	5/8
—1/8	—1/8	—1/8	3/8	5/8	1/8	1/8	3/8	5/8	5/8	1/8	3/8

If these values for p, q and r for all ($= m$) atoms within the fundamental cell be substituted in:

$$S = \sum_m \left(A_n \, . \, e^{2 i \pi (p_m h + q_m k + r_m l)} \right),$$

and if it be taken into account, that for the group T_h^6 all terms containing sinuses are equal to *zero* in the structural factor, — then it is possible to calculate directly for all planes $\{h k l\}$ the intensities of the diffraction-images for all orders.

These values are given in the table on the next page.

It will be clear from this, that there is a fairly good agreement between the calculated and observed intensities from a qualitative point of view, especially if the difficulty be taken into account of avoiding the attribution of a too great relative value in the estimation of the intensities of images, which eventually are excelling by their distinctness.

For it is easily seen, that the estimated intensities in the last column are placed in all cases in just the same sequence of increase, as occurs

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[1]) Instead of *Ge* and *J*, also the values for *Ge*···· and *J'* might have been taken; the differences, however, are not very appreciable in this case.

Table of calculated Intensities

Indices:	Order:	Structural-amplitudines:			Absolute value of $\|S\|^2$	Intensities	
		1st kind *I*-atoms:	2nd kind *I*-atoms;	Ge-atoms:		Calculated:	Estimated on DEBIJE-Film N^0. 18:
(111)	1	0	0	$64.\sqrt{2}$	0.8	1.6	—*)
(111)	2	— 1272	— 424	0	287.6	42.08	10
(111)	3	0	0	$-64.\sqrt{2}$	0.8	0.05	absent
(111)	4	1272	424	— 256	207.4	6.3	3
(111)	5	0	0	$64.\sqrt{2}$	0.8	0.01	absent
(111)	6	— 1272	— 424	0	287.6		—
(011)	1	0	0	0	0	0	—
(011)	2	— 424	+ 424	0	0	0	absent
(011)	3	0	0	0	0	0	„
(011)	4	1272	424	256	381.0	28.1	9
(011)	5	0	0	0	0	0	absent
(011)	6	— 424	+ 424	0	0	0	„
(001)	1	0	0	0	0	0	—
(001)	2	424	— 424	0	0	0	absent
(001)	3	0	0	0	0	0	„
(001)	4	1272	424	— 256	207.4	16.7	7
(112)	1	0	0	— 128	1.6	1.5	very faint
(112)	2	— 424	424	0	0	0	absent
(112)	3	0	0	— 128	1.6	0.1	„
(112)	4	1272	424	256	381.0	15.2	2
(311)	1	0	0	$-64.\sqrt{2}$	0.8	0.4	absent
(311)	2	— 1272	— 424	0	287.6	29.0	8
(331)	1	0	0	$64.\sqrt{2}$	0.8	0.2	absent
(331)	2	— 1272	— 424	0	287.6	14.5	3

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*) If the line was situated outside the efficient part of the film, this is indicated by — in the last column.

with the calculated values; and everywhere the calculated intensities are equal to zero or to extremely small values, if among the observed intensities they were zero in reality. The here adopted structure, therefore, evidently completely accounts for all characteristics of the ROENTGEN-photograms of these crystals.

With respect to the intensity-distribution of the spots in the LAUE-image, which gives the illusion of an apparent symmetry after the planes of {110}, — it may be remarked that in the adopted structure three planes of {110} containing each time 8 *J*-atoms and 2 *Ge*-atoms intersect along each cube-diagonal. In each of these planes the diffractive power of the *J*-atoms strongly dominate that of the *Ge*-atoms. In the structure as a whole, the other *J*-atoms are situated, moreover, symmetrically with respect to these three planes, which is not the case with the *Ge*-atoms, and for the last reason, therefore, the {110}-planes are, in reality, *no* true symmetry-planes of the structure. But just because the diffractive power of the symmetrically distributed *J*-atoms is so strongly predominant in comparison with that of the much more scanty *Ge*-atoms, the influence of the last is practically lost in the LAUE-radiogram. It is for this circumstance, that the LAUE-image on {111} appears to be symmetrical after three planes of {110} and is, therefore, deceptive as a criterion for the symmetry-determination of the crystal.

Finally, we wish to draw attention to the fact, that the results here obtained are in full agreement with R. G. DICKINSON's determinations [1]) of the also dyacisdodecahedral *Tintetraiodide*: $Sn\,I_4$. According to GROTH's measurements this substance, which is isomorphous with $Ge\,I_4$, crystallizes from carbondisulphide in octahedral crystals, showing a combination of: {111}, {210}, {211}, {100}, and smaller: {110}, {120} and a dyacisdodecahedron of the zone [(210) : (111)], which could not be determined more precisely. Also NORDENSKJÖLD [3]) and RETGERS [4]) investigated this compound; the last author observed in crystals from a solution in methylene-iodide also a pentagonal-dodecahedron {210}. The structure deduced by DICKINSON is completely analogous to that adopted here for $Ge\,I_4$; even the dimensions of the fundamental cell (12,23 A.U.) are wholly comparable with those for $Ge\,I_4$. According to the American author a yet better agreement between calculated and observed intensities may be obtained in the case of $Sn\,I_4$, by a slight shift of the *Sn*- and *J*-atoms along a cube-diagonal.

On the contrary, the determinations of MARK and WEISSENBERG [5]) must be considered as quite insufficient. They also observed in their LAUE-radiograms a symmetry with respect to {110} and, moreover, to {100};

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[1]) R. G. DICKINSON, Journ. Amer. Chem. Soc., **45**. 958, (1923).

[2]) P. GROTH, *Chemische Krystallographie*, **1**, p: 231.

[3]) N. G. NORDENSKJÖLD, Bihang K. Vet. Akad. Förh. Stockholm, 2, N⁰. 2, (1874).

[4]) J. W, RETGERS, Zeits. f. Kryst., **22**, 270, (1894).

[5]) H. MARK and K. WEISSENBERG, Zeits. f. Physik, **16**, 18, (1923).

for this reason, they exclude the space-group T_1^h. In the above we have discussed the cause of the appearance of those symmetry-planes parallel to {110} and emphasized, that care must be taken not to be misled by this fact, as the phenomenon is solely a consequence of the predominant diffractive influence of the numerous *I*-atoms, symmetrically arranged with respect to {110}, in comparison with the much less powerful diffraction by the not symmetrically situated *Ge*-atoms. The authors also have taken a value for the cube-edge *a*, which is only half the true one: we have fully discussed, why the fundamental distance *a* needs to be taken twice as great. The measurements and determinations of both investigators are, therefore in full disagreement with the symmetry of SnI_4, as determined by GROTH and others; in accordance with our experiences in the case of GeI_4, there is no reason to doubt the exactness of these older crystallographical data.

Although there is no complete certainty as to the question, whether in the case of GeJ_4 there is present a structure formed by *ions* or not, — it is of interest, however, to draw attention to the fact, that throughout the whole structure tetrahedral groups ($Ge—J_4$) can clearly be discerned as more or less autonomical units in it. In this respect a very recent investigation of HANTZSCH and CARLSOHN [1]) may also be quoted here, in which paper the authors, by demonstrating a number of additive relations between the meltingpoints of the halogenides of the elements in the fourth group of the periodic table, also arrive at the result, that in the crystals of these compounds not the ions, but the molecules themselves are the real structural units.

Groningen, Laboratory for Inorganic and
physical Chemistry of the University.

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[1]) A. HANTZSCH and CARLSOHN, Ber. d. d. chem. Ges., **58**, 1741, (1925).

Physics. "*On the Excitation of Spectrum Lines by Collisions of Electrons*".

By Dr. G. HERTZ. (Communicated by Prof. P. EHRENFEST).

(Communicated at the meeting of October 27, 1923).

According to the theory of quanta it is to be expected that by the collision with an electron an atom is enabled to emit a definite spectrum line only when the kinetic energy of the electron is greater than a certain threshold value, characteristic of the line in question. The potential which an electron must pass through freely to acquire this kinetic energy will be called the excitation potential dependent on the nature of the system emitting the light. In the simplest case of PLANCK's oscillator, the excitation potential is determined by the frequency, and expressed by the equation $Ve = h\nu$. According to BOHR's atomic theory, the work required for the excitation of a definite line, is equal to the energy which must be performed to transfer the atom from its normal state into the highest of the two stationary states between which a transition must take place to give the emission of the spectrum line in question. Hence the excitation potential of a definite spectrum line is given by the equation $Ve = Ie - hT$, in which I represents the ionisation potential, and T the smallest of the two terms characteristic of the spectrum line.

So far the existence of an individual excitation potential has, experimentally, only been shown for the resonance lines of the alkali and earth-alkali metals, and of the metals that are in the same group of the periodic system with these [1]). Also the value of the excitation potential was found to be in agreement with that which is to be expected according to the theory of quanta. This furnished a proof of the quantous character of this phenomenon directly from the experiment: but the results found could teach us nothing about BOHR's atomic model, because for all absorption lines of the atom in its normal state, hence also for the resonance lines, the excitation tension can be derived from the frequency (through the $h\nu$ relation) both when BOHR's atomic model and when PLANCK's oscillator was taken as starting-point. To decide experimentally whether the terms of a series must really be taken as definite values of the energy, as is the case according to BOHR's theory, it is necessary to make observations of the excitation of the higher lines of the spectrum series. The possibility that by collisions of electrons not only quanta of energy corresponding to the frequency of the resonance lines can be transferred, but also such as correspond to the transition of the atom to higher stationary states, has been experimentally shown by J. FRANCK and E. EINSPORN [1]) for mercury, and by J. FRANCK and P. KNIPPING [2]) for helium. As the energy quanta observed here are in very good agreement with the values calculated according to BOHR's theory from the terms of the series, it was very probable that also the emission of the lines corresponding to these terms, will start at the excitation potentials observed. Remarkably enough, however, almost all the observers who of late have investigated directly spectroscopically the excitation of spectrum lines through collisions of electrons, have come to another result. RAU [3]), indeed, found already before, that in helium the excitation potentials become greater for the different terms of a series with ascending number. Likewise RICHARDSON and C. B. BAZZONI [4]) found different excitation potentials for different lines. On the other hand in their experiments on the excitation of light in metal vapours P. D. FOOTE and W. F. MEGGERS [5]) come to the conclusion that the resonance lines from a definite excitation potential (given by the $h\nu$-relation) can be excited without the other part of the spectrum being excited at the same time, but that all the higher lines of the series together do not make their appearance until the ionisation potential is reached. A. C. DAVIES [6]) arrives at the same result for helium and G. DÉJARDIN for helium and mercury [7]). Under these circumstances it seemed to me of interest once more to investigate the excitation of spectrum lines through collisions of electrons by the aid of an arrangement through which surces of error were prevented as much as possible.

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[1]) J. FRANCK and G. HERTZ, Verh. D. Phys. Ges. **16**, 512, 1914.
J. C. MC LENNAN and HENDERSON, Proc. Roy. Soc. **91**, 485, 1915.
J. C. MC LENNAN and H. I. C. IRETON, Phil. Mag. **36**, 461, 1918.
P. D. FOOTE, W. F. MEGGERS and F. L. MOHLER, Phil. Mag. **42**, 1002, 1921; Astroph. Journ. **55**, 145, 1922; Phil. Mag. **43**, 659, 1922.

The method used was in principle the same as is often applied in investigations in this region. The electrons emitted by an incandescent cathode are accelerated by an electric field, and pass through a metal gauze into a fieldfree space, in which they collide with the atoms of the gas or the metal vapour; then it is examined in what way the spectrum of the light emitted in consequence of the collisions depend on the potential which gives the electrons their acceleration. One of the first requirements is that the electrons have as much as possible the same velocity. As the excitation potentials for the different lines often differ only a few tenths of a Volt, a comparatively small irregularity in the velocity is already sufficient to render its determination impossible. Sources of errors which may have an injurious influence in this respect, are: 1. Potential differences between different points of the source of the electrons (gradient of the tension in the incandescent wire). 2. Wide grating instead of a fine gauze. 3. Disturbance through space charges in the observation space in consequence of the use of too great densities of the current. 4. The possibility that the pure electron discharge changes into an arc discharge, to which there is a tendency chiefly in potentials in the neighbourhood of the ionisation potential. These sources of errors are not independent of each other. Thus e.g. the transition to an arc discharg eis promoted by the use of a wide grating, whereas on the other hand the appearance of the arc discharge partially renders the error in consequence of too great gradient of the tension in the incandescent wire ineffectual, because such a low tension arc always takes up a position at a definite point of the incandescent wire. When the spectrum of a low tension arc is observed, it is found that under favourable circumstances we have to do with electron velocities which are pretty equal inter se; they are, however, evidently not yet sufficient to bring out the small differences in the excitation tensions of the higher terms in the series.

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[1]) E. EINSPORN, Zeitschr. f. Phys. **5**, 208, 1921.

[2]) J. FRANCK and P. KNIPPING, Zeitschr. f. Phys. **1**, 320, 1920.

[3]) H. RAU, Sitzungsber. Phys. Med. Gesellsch. Würzburg 1914, pag. 20.

[4]) O. W. RICHARDSON and C. B. BAZZONI, Nature **98**, 5, 1916.

[5]) P. D. FOOTE and F. W. MEGGERS, Bur. Standards Scientif. Paper Nr. 386, 1920.

[6]) A. C. DAVIES, Proc Roy. Soc., **100**, 599, 1922.

[7]) G. DÉJARDIN, C. R. **175**, 952, 1922.

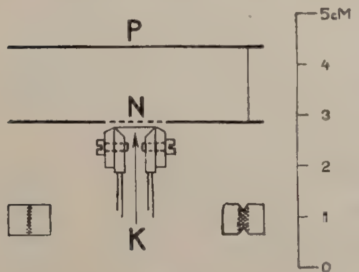

Fig. 1.

To avoid these errors as much as possible an arrangement was used as represented in fig. 1. The incandescent cathode *K*, a thin platinum strip 6 mm. wide provided with a spot of barium-oxide on the upper side, is placed before a gauze *N*, at a distance of about half a mm. The plate *P* is in conducting connection with *N*. In some experiments the space between *N* and *P* was enclosed on all sides with metal walls, with the exception of one slit, in order to obtain a perfectly fieldfree space; the simpler form represented in the figure has, however, also appeared to be sufficient. With this arrangement there was no danger of the transition to an arc charge, even at tensions above the ionisation tension, at the pressures applied, when the meshes of the gauze were taken sufficiently fine and the distance between the incandescent cathode and the gauze sufficiently small. In order to prevent any injurious influence of the gradient of the tension in the incandescent cathode, care was taken that only a narrow strip at right angles to the direction of the heating current emitted electrons, so that there were no potential differences of more than 0.1 Volt between the different points of the source of the electrons. In some experiments this effect was reached in this way that the oxide was added in the form of a transverse strip only $^1/_2$ mm.

broad on the platinum band. The application of such a strip being, however, difficult, the experiment was afterwards made with a larger spot, and a shape was given to the platinum band as drawn in the figure at the bottom on the right. In consequence of the increased current density in the middle a pretty sharp maximum of the temperature is obtained there. In view of the exceedingly great dependence of the electron emission on the temperature this entails that practically the emission issues only from a narrow strip lying in the region of maximum temperature.

To avoid disturbances through space charges the strength of the current was never chosen higher than 10 amp. This is particularly necessary when rare gases are examined, in which case higher pressures must be worked with than with metal vapours on account of the slighter efficiency of the unelastic collisions. Already at small current densities the electrons which are innumerable times knocked to and fro by the gasatoms, cause a considerable space-charge, from which ensues that the space is no longer fieldfree, so that the electrons have different velocities at different places. That this is actually the case may be clearly seen when a tension is applied which is just above the excitation tension of the lines appearing first. Then the space-charge betrays itself by a dark space in the neighbourhood of the greatest density of the electrons (immediately before the gauze). For here the electrons have a smaller velocity than corresponds to the applied tension as a consequence of the negative space-charge.

In experiments where an intensity as great as possible is aimed at, this injurious influence of the space-charges may be obviated by the addition to the gas under examination of a small quantity of another rare gas or metal vapour of which the ionisation tension lies below the lowest excitation tension of the gas under examination. If this is done, there are always some positive ions present, which are just able to compensate the space-charge of the electrons. Of course the pressure of the added gas must not be too great, because else the positive space-charge would become too great and too many electrons would cede their energy to the atoms of the added gas, instead of to that of the gas under examination. It has appeared that mercury vapour with the vapour tension which it has at room temperature, added to neon of a pressure of about 0.8 mm. gives exactly the required effect. In such a tube filled with neon and mercury it is possible to work with currents of some milliampères without being hampered by the space-charge, and then a sufficient intensity is reached to enable us to perform the experiment also by way of demonstration. Particularly suitable for this purpose is a tube filled with a mixture of neon and helium, to which mercury has been added, because such a tube enables us to observe the successive appearance of the lines of mercury, neon, and helium at the corresponding excitation tensions. Also the appearance of the resonance line of mercury at about 5 Volt can be shown with such a tube, as the appearance of this ultra-violet line becomes visible through the fluorescence of the glass wall. In the investigation mentioned the experiment was made without addition of mercury, and the strength of the current was chosen sufficiently small to prevent disturbances through space-charge, this to avoid possible secondary effects, as e.g. action of excited atoms of one kind on those of the other kind. Then the intensity of the excited radiation was comparatively small; the spectrum observations reproduced required an exposure of from 6 to 12 hours.

Already a cursory visual observation taught that all the examined lines of the arc-spectrum of mercury, neon, and helium behave in accordance with the theory of BOHR, as they appear from definite excitation tensions characteristic of the separate lines or groups of lines. Accurate measurements of the excitation tensions have not yet been carried out. For this it is necessary to make measurements about the dependence of the intensity of the lines on the velocity of the electrons. Such measurements are in preparation. In the strongest lines the excitation tension could be measured with the accuracy of some tenths of a Volt, by determining the tension at which these lines suddenly appear. Though the results obtained thus agree very well with the values that can be derived from the values of the terms, yet this method of measurement cannot be considered as reliable in every respect.

Also without measurements of the intensity the successive appearance of the lines can be shown by exciting different tensions smaller than the ionisation tension, and examining the corresponding spectrum. Then, only those lines will be observed of which the excitation tension lies below the excited tension. If this tension is increased by a definite amount, the newly occurring lines must all be lines with higher excitation tension.

As in all measurements on collisions of electrons, the difficulty is also here to know the absolute value of the tension which gives its velocity to the electrons; here too this tension can only be indicated with an accuracy of about 0.5 Volt. For the measurement of the excitation tension the best method is therefore to test the apparatus by means of a gas, the excitation tensions of which can be calculated from the spectrum series, as this has been done more than once in measurements of excitation tensions by the electric method. On account of this uncertainty in the absolute values, the values of the tension that corresponds with the actual velocity of the electrons have been derived in what follows from the calculated excitation tensions of the occurring resp. missing lines. The difference between the indicated values and the tensions read on the Voltmeter was between 1,5 Volt and 2 Volt in all cases; it was accordingly really found through direct measurements of the velocity of the electrons (application of a retarding electric field in vacuum) that the correction to be applied must lie between these limits. It may, therefore, be concluded from the data communicated below that the absolute values agree with an accuracy of 0,5 Volt with those which are calculated from the ionisation tension and the values of the terms according to BOHR.

In the figures 2, 3, and 4 a series of spectra have been reproduced excited in mercury, helium, and neon through the collisions of electrons with different velocities. The times of exposure in mercury and helium have been chosen so that the strongest lines, which also appear already at lower tensions, have about the same intensity on the two representations. The values which are put after the wave-lengths between brackets denote the excitation tensions calculated from the ionisation tension and the values of the terms. The observations with mercury (fig. 2) have been made at a pressure of about 0,03 mm. (the vapour tension at about 60°). It is seen that at lower tension only lines with an excitation tension smaller than 8 Volt appear, the lines that make their appearance on increase of the tension all having a higher excitation tension. Particularly striking is the behaviour of the strong line 3650, which is by

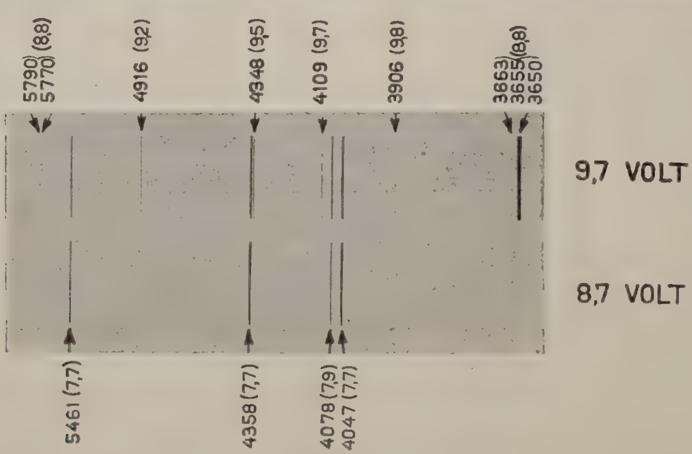

Fig. 2.

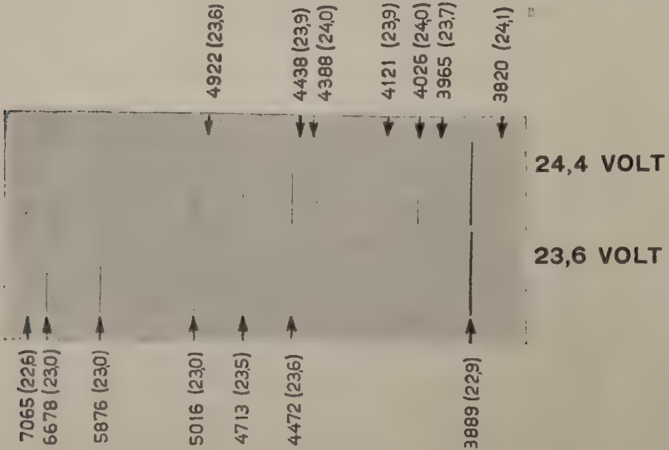

Fig. 3

far the strongest line at the higher tension, and is entirely wanting at the lower tension.

The helium lines behave in the same way (fig. 3). The reproduced spectrum photographs have been made for a pressure of 0,8 mm. From experiments made since then it has appeared that it is more profitable to work with lower pressures; and it seems that to effect a sharp excitation of the lines, still smaller current densities should be used in helium than e.g. in neon. It is impossible that here the formation of metastable helium atoms still plays a part. With sufficiently small current densities the different lines can be made to appear successively also in helium, in correspondence with the successive order of their excitation tensions. Hence here too there is a very good agreement with the values calculated according to Bohr, as appears from the spectograms.

In neon the pressures worked with were between 0.5 and 1 mm. Fig. 4

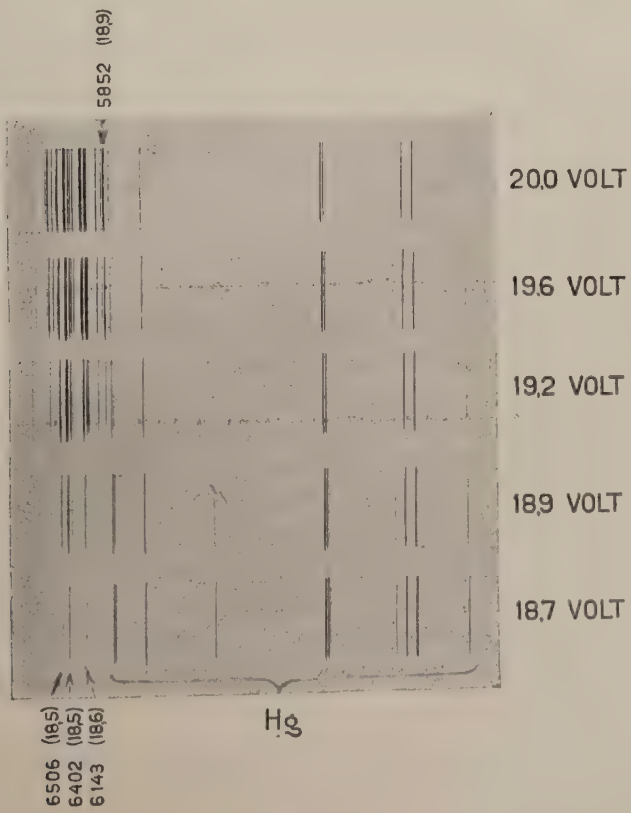

Fig. 4.

gives a series of photographs which show the development of the group of the red neon lines on increasing velocity of the colliding electrons. These observations were made in the presence of a drop of mercury in the tube, but the phenomenon is exactly the same without mercury. Special attention should be given to the behaviour of the yellow neon line 5852, which under normal circumstances is by far the strongest line of the neon spectrum. According to the scheme of the series, as given by PASCHEN ¹) for neon, this line must have an excitation tension which is 0.4 Volt higher than that of the lines 6143, 6402 and 6506; and the yellow line is, indeed, entirely absent at the lowest tension required to excite the said lines; only on increase of the tension by some tenths of a Volt does it make its appearance, and on further increase it soon exceeds the other lines in intensity.

Within the limits of the experimental errors the absolute value of the excitation tensions of these lines are in harmony with the values which can be calculated from the terms of the series and the values found by the writer of this paper for the ionisation tension ²); thus the measurements of the excitation and the ionisation tensions are confirmed by the observations on the excitation of the spectrum lines.

Similar observations were also made with zinc and thallium vapour, which, however, bear a preliminary character. In order to avoid the difficulties met with, when the whole apparatus is brought to a high temperature, a method was applied in which the apparatus could remain at room temperature. For this purpose the apparatus was filled with helium and neon of a pressure of some mm., after which the metal under investigation was brought to evaporation in the fieldfree space between the plates. Thus the result was reached that both the electrons and the metal atoms diffuse through the rare gas, and finally arrive on the surface of the metal after numerous collisions. In this the circumstances can be chosen so that the number of collisions between electrons and metal atoms is great enough to bring about such an intensity of the light excited by these collisions that it can be observed with the spectroscope. So far these experiments have remained restricted to subjective observations with the spectroscope. With a suitable choice of the tension a spectrum could be obtained from zinc consisting only of the triplet 5680, 4722, 4811, while the strong red line 6362 did not make its appearance until the tension had been raised by 1 Volt.

In thallium 3,5 Volt was measured as excitation tension of the green line. This confirms that in thallium the $2p_2$ state is the normal condition, as also GROTIAN ³) has succeeded in showing by means of absorption measurements.

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¹) F. PASCHEN, Ann. d. Phys. **60**, 405, 1919.

²) G. HERTZ, These Proceedings **25**, 179; Zeitschr. f. Phys. **18**, 307, 923.

³) W. GROTRIAN, Zeitschr. f. Phys. **12**, 218, 1922.

Botany. — *"The connection between lightgrowthresponse and phototropical curvature of seedlings of Avena sativa."* By C. VAN DILLEWIJN. (Communicated by Prof. F. A. F. C. WENT).

(Communicated at the meeting of September 26, 1925).

According to the theory of BLAAUW the phototropical curvature of a unilaterally illuminated organ is the result of the difference in lightgrowthresponse induced in the various parts of that organ.

If, for instance, a coleoptile of Avena is subjected to the action of onesided light, there will be a decrease in the quantity of light from the lighted to the unlighted side. As every quantity of light induces a certain lightgrowthresponse, the various parts of the coleoptile will respond differently, causing a phototropical curvature.

As the greatest difference in the quantity of light is found between the proximal and distal sides, these sides will also show the greatest difference in growthresponse, and will be of the greatest importance for the appearance of the phototropical curvature.

BLAAUW[1]) examined a number of objects and proved that organs which exhibit a phototropical curvature also show a typical lightgrowthresponse when subjected to omnilateral illumination, while organs which do not respond to unilateral illumination show no lightgrowthresponse.

The sporangiophore of Phycomyces and the hypocotyl of Helianthus belong to the first, the roots of Avena and Raphanus to the second group. The lightgrowthresponse of Avena was first examinated by VOGT[2]) and later by SIERP[3]), LUNDEGÅRDH[4]) and KONINGSBERGER[5]).

For all these objects it has been demonstrated that phototropical sensibility and lightgrowthresponse go together.

If the theory of BLAAUW *is correct it must be possible to deduce the phototropical curvature from the lightgrowthresponse of proximal and distal sides.*

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[1]) BLAAUW, A. H., Licht und Wachstum I Zeitschr. f. Bot. 6, 1914.
" " " II " " " 7, 1915.
" " " III Mededeelingen van de Landbouwhoogeschool Wageningen 15, 1918.

[2]) VOGT E., Über den Einflusz des Lichtes auf das Wachstum der Koleoptile von Avena sativa. Zeitschrift f. Botanik 7, 1915.

[3]) SIERP, H., Untersuchungen über die durch Licht und Dunkelheit hervorgerufenen Wachstumsreaktionen bei den Koleoptilen von Avena sativa u.s.w. Zeitschr. f. Botanik 13, 1921.

[4]) LUNDEGÅRDH, H., Ein Beitrag zur Analyse des Phototropismus. Arkiv f. Botanik 1922.

[5]) KONINGSBERGER, V. J., Tropismus und Wachstum, Rec. des Trav. bot. Néerl. XIX 1922.

BLAAUW [1]) demonstrated this for the hypocotyl of Helianthus and found that the real phototropical curvature corresponds with the curvature deduced from the lightgrowthresponse.

VAN DE SANDE BAKHUYZEN [2]) has tried to do the same for the coleoptile of Avena. He used the lightgrowthresponses found by VOGT and SIERP. He assumed rather arbitrarily the proportion of 4 : 1 for the quantities of light acting on the proximal and distal sides and then calculated the curvatures which would appear on unilateral illumination. He compared these with the curvatures found by ARISZ.

It will be proved afterwards that the distal side receives far less than $^1/_4$ of the light received by the proximal side.

The connection between lightgrowthresponse and phototropical curvature for Avena was examined experimentally by LUNDEGÅRDH, who opposes BLAAUW's theory because of the results he obtained.

SIERP, who especially studied the lightgrowthresponse, has also considered the connection between lightgrowthresponse and phototropical curvature and with RENNER [3]) declares himself in favour of BLAAUW's theory.

BRAUNER [4]) compared the course of phototropical curvature with the course of the lightgrowthresponse of the proximal side. It will be evident afterwards that the response of the distal side has a great influence on the nature of the curvature and may not be neglected.

I have determined the lightgrowthresponse to a number of different quantities of light and also the lightgrowthresponse to $^1/_{30}$ of these quantities which corresponds to the quantity of light received by the distal side. In each case I compared the curvature deduced from the combination of these two lightgrowthresponses with the phototropical curvature found by ARISZ [5]).

A brief account of the main results is given below. For further details I refer to a publication which will appear later.

The distribution of light.

The distribution of light in the coleoptile was determined with the photographical method, also used by BLAAUW in his study of the hypocotyls of Helianthus: an oblique sagittal section is placed on a sensitive photographic plate and illuminated from above.

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[1]) BLAAUW, A. H., Licht und Wachstum II. Zeitschrift f. Botanik 7, 1915.

[2]) BAKHUYZEN, H. L. VAN DE SANDE, Analyse der fototropische stemmingsverschijnselen, Diss. Utrecht 1920.

[3]) RENNER, O., Die Wachstumsreaktionen bei Licht- und Schwerkraftreizung. Zeitschrift f. Botanik 14, 1922.

[4]) BRAUNER, L., Lichtkrümmung und Lichtwachstumsreaktion. Zeitschrift f. Botanik 14, 1922.

[5]) ARISZ, W. H., Untersuchungen über den Phototropismus. Rec. des Trav. bot. Néerl. 12, 1915.

The decrease of light for Avena appeared to be far greater than for Helianthus. The distal side receives only $^1/_{30}$ of the quantity of light received by the proximal side.

This is mainly due to the presence of the primary leaf, which absorbs the greater part of the light. (Fig. 1).

More light passes through where this leaf ends (about $^1/_2$ mm from the apex). In this part the distribution of light is very complicated, which is mainly due to the paraboloid form of the apex. I have assumed the light proportion of 30 : 1 for the whole coleoptile in my experiments. If further investigations should prove that the influence of the apex may not be neglected, I will have to compare the phototropical curvatures calculated from the lightgrowthresponse with the curvatures of the coleoptile in the apex of which the light proportion of 30 : 1 has been caused artificially. This can be achieved by bringing a smoked piece of glass in a median incision in the apex. Everywhere in these coleoptiles there will actually be a lightproportion of 30 : 1.

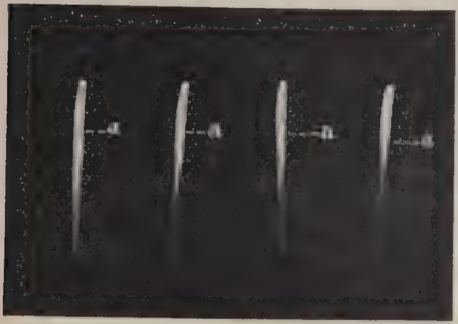

Fig. 1. The sections from left to right are illuminated by increasing quantities of light. It is obvious that a fair amount of light passes when only the coleoptile is present. Most of the light is absorbed in the part where the primary leaf is present.

a indicates the place where the section begins.

The lightgrowthresponse.

The lightgrowthresponse was determined with the auxanometer of KONINGSBERGER [1]) by which the growth is recorded automatically while the plant grows in the dark. As a source of light a PHILIPS "Argenta" electric lamp was fixed above the plant. The light was reflected onto the coleoptile by three mirrors which were placed at an angle of 45°. The coleoptile was protected against direct light from above by a round piece of card-board between lamp and coleoptile. The temperature of the darkroom was 20° C. The relative humidity varied between 65 $^0/_0$ and 70 $^0/_0$. The growth was recorded for a few hours and only after the growth remained constant for an hour or more the coleoptile was illuminated.

Four series of lightgrowthresponses were determined, three with the intensity of 2400 M. C. and 80 M. C. and one with 80 M. C. and

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[1]) KONINGSBERGER, V. J., Tropismus und Wachstum. Rec. des Trav. Bot. Néerland. Vol. XIX 1922.

2.5 M. C. The lightgrowthresponse was determined for each quantity of light about 6 times and the average taken.

15 min. × 2400 M.C.
15 min. × 80 M.C.

Graph *a* in fig. 2 gives the lightgrowthresponses to these quantities. In all the graphs the great period is taken into consideration and only changes in the rate of growth, as result of the illumination, are reproduced. In graph *a* both reactions are about the same; a minimum of growth is reached after about half an hour and a maximum after about 50 min. The responses differ however in the rate of growth. On illuminating with 2400 M.C. the growth remains constantly less than on illuminating with 80 M.C. If this is applied to a coleoptile illuminated unilaterally with 15 min. × 2400 M.C., the distal side will grow quicker than the proximal side, and we may expect a positive curvature.

Arisz actually found a positive curvature for this quantity (2.160.000 M. C. S.).

90 sec. × 2400 M.C.
90 sec. × 80 M.C.

These quantities give about the same result as the first. The only difference is that the minimum and maximum are reached sooner owing to the shorter period of illumination. This difference becomes even greater in the following experiments, where the coleoptile was illuminated during 10 sec. Graph *b* shows that the lightgrowthresponse to 2400 M.C. is greater than the response to 80 M.C. As the difference is even greater than in the first experiment we may expect a stronger positive curvature.

Arisz did not determine the curvature for the same quantity of light (216000 M.C.S.) In the case of 162000 M.C.S. and 240.000 M.C.S. he found a positive curvature.

10 sec. × 2400 M.C.
10 sec. × 80 M.C.

Graph *c* illustrates the responses to these quantities. This experiment shows that the response to 2400 M. C. is totally different from the response to 80 M.C., whereas in the first two experiments there was only a difference in the rate of growth.

The response to 2400 M.C. is about the same as in the previous experiments except that the minimum is reached sooner (after 23 min.) owing to the shorter period of illumination. The response to 80 M.C. is quite different; the rate of growth decreases slowly and only reaches a minimum after 78 minutes. The maximum growth is attained after 108 minutes. The proximal side of a coleoptile subjected to a unilateral illumination of 10 sec. × 2400 M.C. will give a "short" growthresponse, the distal side a "long" response. The result will be a faint positive curvature, which changes into a stronger negative one after $^1/_2$ hour.

It is also possible that the difference in the rate of growth during the first half an hour is not great enough to cause a noticeable positive

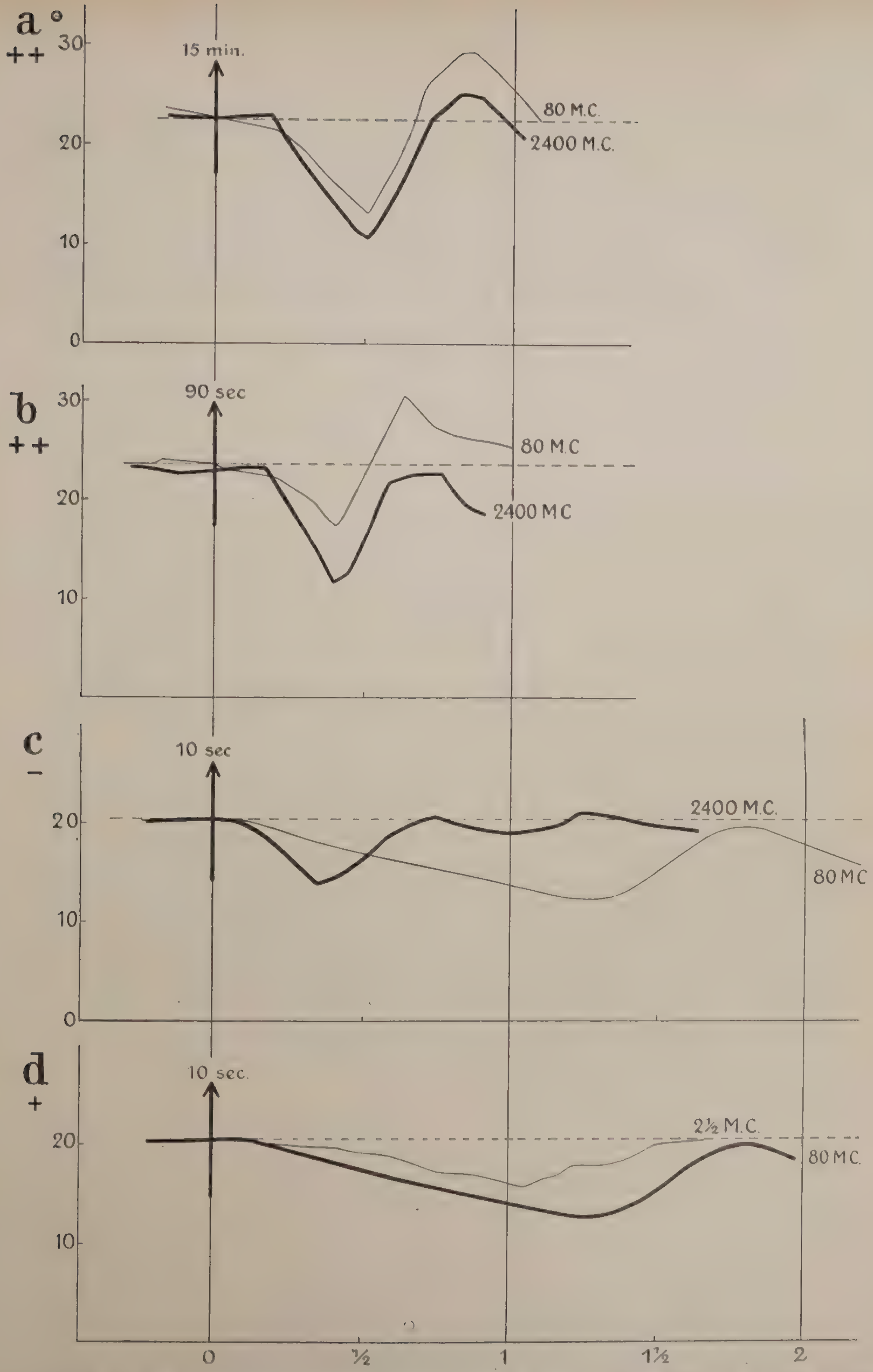

Fig. 2. In the above graphs abscissa represent time in hours and the ordinates rate of growth in μ pro minute. The intensity of light is indicated in M.C.

+ means the area of the first positive curvature

— that of the negative and ++ that of the second positive curvature.

The arrow indicates the moment of illumination.

curvature, and hence only the negative curvature would be visible. ARISZ found negative curvatures in response to 13500 M.C.S. and 27000 M.C.S. With the same quantities of light but with very high intensities he found a positive instead of a negative curvature. This is easily explained as my experiments demonstrated that the "long" response only occurs with low intensities. The distal side will also show a "short" response to high intensities and a positive curvature as in graph *a* and *b* would occur.

10 sec. × 80 M.C.
10 sec. × 2.5 M.C.

Both quantities give a "long" response but the response to 80 M.C. is greater than the response to 2.5 M.C. Hence a coleoptile illuminated unilaterally with 10 × 80 M.C. will show a positive curvature. ARISZ actually found a positive curvature in responce to this quantity.

On examining the responses in fig. 2 it will be obvious that the curvature deduced from them must be positive with the smallest quantity of light (*d*), negative with greater quantities (*c*), and when the quantity increases again positive (*b*) gradually becoming fainter as the quantity is further increased (*a*). ARISZ in his research about the phototropical curvature of Avena also found three areas of curvatures: one of the first positive curvature, one of the negative curvature, and one of the second positive curvature, according to the increasing quantity of light.

Hence the curvatures deduced from the lightgrowthresponse of proximal and distal sides correspond with the real curvatures observed by ARISZ.

ARISZ found a peculiarity in the phototropical curvatures which he could not explain. He observed that no negative curvature is obtained with low light intensities, no matter how long the illumination lasts. This fact is easily explained by means of the lightgrowthresponse, as low intensities call forth a "long" response of the proximal and distal sides (graph *d*) causing a positive curvature. A negative curvature only appears when the proximal side gives a "short" response and this is obtained only with a certain intensity. No negative curvature will occur below this intensity.

Utrecht, September 1925. *Botanical Laboratory.*

Physics. — *"On the Relation of the Internal Latent Heat of Evaporation to the Molecular Surface Energy, in Connection with the Modified Law of the Corresponding States"*. By Dr. J. J. VAN LAAR. (Communicated by Prof. H. A. LORENTZ).

(Communicated at the meeting of September 26, 1925).

I.

These Proceedings, 28, p. 356 contain an interesting article by Mr. VAN URK on the limiting value of the above relation at the absolute zero, for which he theoretically finds the value 4 for simple substances. For oxygen, argon and nitrogen this value is about confirmed; for the values found for these substances are resp. 3,75, 4,0 and 3,9. But for hydrogen 2,6 is found, and for Helium a still smaller value, i.e. 1,8, would have been found. And for the large category of the so-called „ordinary" substances everywhere values are found in the neighbourhood of 5,3 (as against 7 for $T = {}^1/_2 T_k$). These values already indicate that the relation in question is by no means constant, but that in a way, which will be more closely defined later, the value will depend on the *family* of substances that is considered, and which is characterized by the value of the *parameter* γ, i.e. of the reduced coefficient of direction of the straight line between ${}^1/_2\, d_0$ en d_k, when d_0 and d_k represent the reduced liquid densities resp. at $T = 0$ and $T = T_k$.

It is, indeed, easy to derive a general formula for the ratio $\lambda : \mu$, from which it will then appear that this ratio with close approximation will be $= f$ for $T = {}^1/_2 T_k$, f being the so-called vapour-pressure factor at this temperature in the well-known vapour pressure formula

$$log \frac{p_k}{p} = f\left(\frac{T_k}{T} - 1\right),$$

and that this ratio approaches to ${}^1/_2\, f_0$ at $T = 0$, in which f_0 is the extrapolated limiting value of f at $T = 0$. (For hydrogen to $0{,}8\ f_0$).

II.

We start from the relation (valid for temperatures, at which the vapour density may be neglected in comparison with the liquid density) for the surface tension σ:

$$\sigma = \frac{a}{v^2}\, u,$$

in which u (compare also Chemisch Weekbl. **15** (1918), p. 694 et seq.[1]) is a quantity of linear dimensions of the order of magnitude of the mean distance between two neighbouring molecules. Hence we may write for u:

$$u = \frac{1}{x} \left(\frac{v}{N} \right)^{1/3},$$

in which $v = M:D$ is the volume of a gramme-molecule of the liquid (M is the molecular weight, D the density) and N the number of molecules in a gramme molecule. In consequence of this σ becomes:

$$\sigma = \frac{1}{x} \frac{a}{v^2} \left(\frac{v}{N} \right)^{1/3},$$

hence the molecular surface energy $\mu = \sigma v^{2/3}$:

$$\mu = \frac{1}{x} \frac{a}{v} \frac{1}{N^{1/3}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

At the time (loc. cit. p. 695—696) we found for the values of x values which all lie in the neighbourhood of 7, that is for ordinary substances and at $T = {}^1\!/_2\, T_k$. But it is clear that for other substances and at other temperatures the value of x will appear to be very different.

Further

$$\lambda = \frac{a}{v} (1 + \theta) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

holds for the internal latent heat of evaporation, when the vapour density may be neglected by the side of the liquid density; in which equation the correction quantity θ refers to the variability of a with the temperature[2]), and is a small positive quantity for all substances, except for hydrogen and helium. For H_2 and He the value of θ $\left(= -\frac{1}{2} \frac{T}{a} \frac{da}{dt} \right)$ is negative, because there at lower temperatures a increases with t instead of decreasing (see my book „Die Zustandsgleichung etc.", p. 232—239). For $T = 0$ θ will be $= 0$, because a will no longer vary with t at very low temperatures. Hence we have:

$$\frac{\lambda}{\mu} = x (1 + \theta) N^{1/3},$$

and therefore

$$\underline{x (1 + \theta) = \frac{\lambda}{\mu} : N^{1/3}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

For the second member VAN URK also writes (p. 354) $\frac{\lambda : N}{\mu : N^{2/3}} = \frac{\lambda'}{\mu'}$, in which λ' and μ' represent the quantities λ and μ *per molecule*.

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[1]) See also ibid. **15**, 680 (1918) and **16**, 3 (1919).

[2]) The variability of a with the volume is neglected, because else λ would not be $= \frac{a}{v} \times$ etc.

III.

Let us now calculate the values of λ and μ from known formulae. From the general relation

$$L=T\,(v_2-v_1)\frac{dp}{dt}=Tv_2\frac{dp}{dt},$$

when the liquid volume v_1 may be neglected by the side of the vapour volume v_2, follows

$$L=\frac{T}{p}\frac{dp}{dt}\,.\,pv_2=RT\,.\,\frac{T}{p}\frac{dp}{dt},$$

because at lower temperatures also $pv_2=RT$; so that

$$\lambda=RT\left[\frac{T}{p}\frac{dp}{dt}-1\right]\,.\;.\;.\;.\;.\;.\;.\;.\;.\quad(4)$$

is found for

$$\lambda=L-p\,(v_2-v_1)=L-pv_2=L-RT.$$

Now from

$$\log\frac{p_k}{p}=f\left(\frac{T_k}{T}-1\right),$$

in which f is a slight function of the temperature, follows immediately (cf. also Zust.gl., p. 228 et seq.):

$$-\frac{1}{p}\frac{dp}{dt}=-\frac{fT_k}{T^2}+\left(\frac{T_k}{T}-1\right)\frac{df}{dt}.$$

Hence

$$\frac{T}{p}\frac{dp}{dt}=f\frac{T_k}{T}-\left(\frac{T_k}{T}-1\right)T\frac{df}{dt},$$

or with $T:T_k=m$ and $\frac{df}{dt}=\frac{1}{T_k}\frac{df}{dm}$:

$$\frac{T}{p}\frac{dp}{dt}=\frac{f}{m}-\left(\frac{1}{m}-1\right)m\frac{df}{dm}=\frac{f}{m}-(1-m)f'_m\,.\;.$$

As $T:m=T_k$, (4) becomes therefore:

$$\underline{\lambda=RT_k\left[(f-m)-m\,(1-m)\,f'_m\right]}\;.\;.\;.\;.\;.\;.\;.\quad(5)$$

Further we have according to the well-known equation of EÖTVÖS:

$$\underline{\mu=\varphi\,(T_k-T)=\varphi T_k\,(1-m)},\;.\;.\;.\;.\;.\;.\;.\;.\quad(6)$$

so that equation (3) passes into

$$\underline{x\,(1+\theta)=\frac{\lambda'}{\mu'}=\frac{R}{\varphi}\,\frac{(f-m)-m\,(1-m)\,f'_m}{1-m}\cdot\frac{1}{N^{1/3}}},\;.\;.\;.\quad(7)$$

in which φ generally lies in the neighbourhood of 2. At low temperatures the value of x will therefore be chiefly determined by f, which value — as we remarked above — will be *different for every category of substances*, dependent on the value of the parameter γ[1]).

IV.

We will now further reduce the above formula. For R we may write $83{,}17 \,.\, 10^6$ Ergs/Gr.mol., while $N^{1/3} = \sqrt[3]{0{,}6060 \,.\, 10^{24}} = 0{,}8462 \,.\, 10^8 =$ $= 84{,}62 \,.\, 10^6$, so that $R : N^{1/3}$ becomes $= 1 : 1{,}0175$.

For *ordinary* substances on an average 2,10 is found for φ (benzene 2,104, $CHCl_3$ 2,013, CCl_4 2,105, Ether 2,172, etc.), while on an average 1,98 is found for argon, nitrogen, and oxygen (argon 2,02, N_2 2,002, O_2 1,917). Hence φ (except for H_2 and He) may be put at 2,04, and as $(1 : 1{,}0175) : 2{,}04 = 0{,}48 = 0{,}5$, we may write:

$$x\,(1+\theta) = \frac{\lambda'}{\mu'} = 0{,}5\,\frac{(f-m) - m\,(1-m)\,f'_m}{1-m}, \quad . \quad . \quad . \quad (7a)$$

in which the factor 0,5 passes into 0,76 for H_2, where $\varphi = 1{,}294$.

We shall now examine this formula more closely for the case $m = {}^1\!/_2\,(T = {}^1\!/_2\,T_k)$ and for $m = 0\,(T = 0)$.

a. $m = {}^1\!/_2$. That the formula for this case leads to good results, may appear from what follows.

1. In *benzene*, a member of the extensive family of the *ordinary* substances, $f'_m = T_k\,f'_t$ lies in the neighbourhood of $562 \times (-0{,}0038) = -2{,}1$ for $m = 0{,}5$ (8° C.) (See Zust. Gl. p. 222), so that $m(1-m)\,f'_m$ becomes $= -\,0{,}5$. Consequently the numerator becomes $= f - 0{,}5 + 0{,}5 = f$, and therefore

$$\frac{\lambda'}{\mu'} = 0{,}5\,\frac{f}{0{,}5} = f \text{ (ordinary substances)} \quad . \quad . \quad . \quad . \quad (8)$$

According to the table in Zust.Gl. p. 222 the value of f is equal to 6,8 for $m = {}^1\!/_2$.

If λ is calculated directly from the vapour pressures[2]) — which calculation must of course also be made according to (4) or (5), in which at higher temperatures $p(v_2 - v_1)$ must be substituted for RT — then 6,7 is obtained (see the table in Z.Gl. p. 259). The small difference is owing to this, that in formula (7) φ for benzene is not $= 2{,}04$ but $= 2{,}1$, so that 6,8 will become somewhat smaller, and that besides a slight error in f'_t appears augmented in f'_m through multiplication by T_k.

2. For *argon* (Z.Gl. p. 227) the value of f'_t (extrapolated) is clearly

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[1]) Compare about this — in extension of what VAN DER WAALS wrote about this already before — my Papers in These Proc. **16** (1914), p. 808, and Zust. Gl. p. 128 et seq. and 140 et seq. There the whole development of this important subject will be found.

[2]) I have repeated these calculations, and also those with $m = 0$ in V with the greatest accuracy.

negative, and greater (negative) than $-0,005$, so that $f'_m > 151 \times (-0,005)$ or $> -0,75$, hence $m(1-m)f'_m$ greater than $-0,2$. Here $\frac{\lambda'}{\mu'}$ becomes therefore $> f - 0,5 + 0,2$, i.e. $\underline{> f - 0,3}$. As according to the table on p. 227 loc. cit. $f > 5,34$, $\lambda' : \mu'$ will certainly be > 5. The direct calculation from the values of λ' given by VAN URK yields for $m = 0,5$ the value $\underline{5,3}$ (v. U. p. 357).

3. According to the table on p. 228 (Z.Gl.) f'_t is *positive* for *hydrogen* all through, without minimum in the values of f. For $m = {}^1/_2$ (16°,6 abs.) f'_t is about $+0,043$, hence $f'_m = 33,18 \times$ ibid $= + 1,43.$, so that the value 0,36 would follow for $m(1-m)f'_m$ with $m = 0,5$. Hence here:

$$\frac{\lambda'}{\mu'} = 0.76 \frac{f - 0,86}{0,5} = \underline{1,52\,(f - 0,86).}$$

With $f = 3,88$ at $m = 0,5$ (Z.Gl. p. 228) this gives for $\lambda' : \mu'$ the value 4,59. The deviation from the law of BOYLE amounting, however, to 4% at 17°, this becomes $\underline{4,4}$.

According to the values of λ given by VAN URK (p. 356), $\lambda' : \mu'$ would become $= 4,0$. This difference repeating itself also for $m = 0$, the values of λ, given at lower temperatures, or else the formula given for μ, may possibly not be entirely correct.

b. $\underline{m = 0}$. Formula (7^a) then passes into

$$\underline{x_0 = \frac{\lambda'}{\mu'} = 0,5\, f_0,} \quad \ldots \ldots \ldots \quad (9)$$

where for *hydrogen* (see above) the coefficient 0,76 will have to be substituted for 0,5.

For the value of f_0 we have derived the formula (Z.Gl. p. 236):

$$f_0 = \frac{(\gamma+1)^2}{4\gamma}(8\gamma - 1)\frac{a_0}{a_k} \quad \ldots \ldots \ldots \quad (10)$$

In this $f_k - 1$ may be written for $8\gamma - 1$, as f_k, i. e. the value of f at the critical temperature, is always $= 8\gamma$. Further $(\gamma + 1)^2 : 4\gamma = 1$ for nearly all substances [$4 : 4 = 1$ for $\gamma = 1$; $3,61 : 3,60 = 1$ for $\gamma = 0,9$; even $49/16 : 3$ is only little greater than 1 for $\gamma = 0,75$], hence in approximation

$$f_0 = (f_k - 1)\frac{a_0}{a_k}; \quad x_0 = \frac{\lambda'}{\mu'} = \frac{1}{2}(f_k - 1)\frac{a_0}{a_k} \quad \ldots \ldots \quad (11)$$

may be written.

Only for hydrogen will the fore-factor be somewhat different.

1. For ordinary substances ($\gamma = 0,9$ to 1) x_0 lies, therefore, between 3,1 to 3,5 times $a_0 : a_k$. The latter ratio is at least 1,6 (Z.Gl. p. 251 and p. 255; the values given there are those of $a_{1/2} : a_k$, not those of $a_0 : a_k$), so that x_0 becomes $=$ from 5 to 5,6. For benzene ($\gamma = 0.97$) the value $x_0 = \underline{5,3}$ is found directly by extrapolation from the values of λ (Z.Gl. p. 259).

2. For *argon* ($\gamma = 0,75$), *oxygen*, and *nitrogen* ($\gamma = 0,8$) the value $x_0 = {}^1\!/_2 \times 5$ to $5,4 \times 1,5 =$ from 3,75 to 4, with $a : a_k = 1,5$ and $f_k = 6$ to 6,4. From the values of λ the following values are actually found: $\underline{3,9}$ for argon, $\underline{4,0}$ for nitrogen and $\underline{3,75}$ for oxygen. These values are, accordingly, close to 4, but this is in my opinion to be attributed more to purely accidental circumstances than to a theoretical property.

3. For in *hydrogen* everything is again different. Here with $\gamma_{th.} = 0,61$ the value of $(\gamma + 1)^2 : 4\gamma = 1,06$, hence $x_0 = 0,76 \times 1,06 \times 3,88 \times 0,9$, as $f_k = 8\gamma = 4,88$, and $a_0 : a_k = 0,9$ or still slightly less, as for hydrogen the value of a below T_k at first remains about constant when the temperature becomes lower, whereas at lower temperatures it gradually decreases. (For Helium $a_0 : a_k$ is already $< 0,7$; see Z.Gl. p. 249 and 250). Accordingly we find at most $x_0 = \underline{2,8}$. From the extrapolated value of λ_0 is found 2,6, which is again somewhat lower (see above). But at any rate not 4.

Recapitulating all this, we get the following survey, in which the values of $\lambda' : \mu'$ at T_k have been determined from the values of λ in the neighbourhood of T_k given by VAN URK, and as regards benzene, from these calculated by me in Z.Gl. p. 259.

	$T = 0$	$T = {}^1\!/_2\, T_k$	T somewhat $< T_k$
Ordinary substances	$\lambda' : \mu' = 5,3$	7	± 50
Argon etc.	3,9	5,3	± 30
Hydrogen	2,8	(<) 4,4	± 10

It follows from all this that there can be no question of a general limiting value 4 at $T = 0$ (Compare also the *Appendix*).

V.

Some Experimental Data.

From the equation of the straight diameter $d_1 + d_2 = d_0 - 2\gamma m$, when at lower temperatures d_2 may be neglected compared with d_1, follows $d_1 = d_0 - 2\gamma m$, or with $d_1 = v_k : v$ (for d_1 is the reduced liquid density):

$$\frac{1}{v} = \frac{1}{v_0} - \frac{2\gamma}{v_k}\, m = \frac{1}{v_0}\left(1 - 2\gamma\, \frac{v_0}{v_k}\, m\right).$$

But $v_k : v_0 = d_0$, and $d_0 = 2\,(1 + \gamma)$, hence:

$$\frac{1}{v} = \frac{1}{v_0}\left(1 - \frac{\gamma}{1+\gamma}\, m\right).$$

[That $d_0 = 2\,(1 + \gamma)$, follows immediately from the equation for the straight diameter, which becomes $2d_k = d_0 - 2\gamma$ for $m=1$, hence because $d_k = 1$, d_0 will be $= 2(1+\gamma)$].

If a were constant, $\frac{a}{v}$ would also be $\frac{a}{v} = \frac{a}{v_0}\left(1 - \frac{\gamma}{1+\gamma} m\right)$, but since a is always $< a_0$ (except for H_2 and He), we get:

$$\frac{a}{v} = \frac{a_0}{v_0}\left(1 - \varepsilon \frac{\gamma}{1+\gamma} m\right),$$

in which ε is a factor > 1, except for H_2 and He, where ε will be slightly < 1. And since $\lambda = \frac{a}{v}(1+\theta)$, in which $\theta = 0$ for $m=0$ and positive for $m > 0$ (negative for H_2 and He, see § 2), it follows that with $\frac{a_0}{v_0} = \lambda_0$:

$$\frac{\lambda}{1+\theta} = \lambda_0 \left(1 - \varepsilon \frac{\gamma}{1+\gamma} m\right),$$

or

$$\lambda = \lambda_0 \left(1 - \varepsilon' \frac{\gamma}{1+\gamma} m\right),$$

in which ε' will be somewhat smaller than ε (for H_2 and He somewhat larger).

a. From the experimental results for benzene (Z.Gl. p. 259) follows with $T_k = 561{,}6$:

$$\lambda = 12770 - 17\,T = 12770\,(1 - 0{,}001332\,T),$$

hence also

$$\lambda = 12770\,(1 - 0{,}748\,m) \text{ (in gr. kal. per gr. mol.).}$$

Now $\gamma = 0{,}973$, hence $\gamma : (1+\gamma) = 0{,}493$, so that the value $\underline{1{,}52}$ is found for the factor ε', which corresponds to the variability of a with t.

For μ holds:

$$\mu = 2{,}104 \times 561{,}6\,(1-m) = 1182\,(1-m),$$

so that $\left(\frac{\lambda}{\mu}\right)_{0,5} = \frac{7990}{591} = 13{,}53$ is found for $m = 0{,}5$.

Now $\frac{\lambda'}{\mu'} = \frac{\lambda}{\mu} : N^{1/3}$ (see § 2), so that we must still divide by $84{,}62 \,.\, 10^6$ (see § 4). But in order to reduce Gr. cal. to ergs we must multiply by $41{,}863 \,.\, 10^6$; hence we must finally divide by $2{,}0212$. Therefore we find for benzene:

$$\left(\frac{\lambda'}{\mu'}\right)_{1/2} = \frac{13{,}53}{2{,}021} = 6{,}69 = 6{,}7.$$

And for $m = 0$ $\left(\frac{\lambda'}{\mu'}\right)_0$ will become:

$$\left(\frac{\lambda'}{\mu'}\right)_0 = \frac{12770}{1182} : 2{,}021 = 5{,}34 = 5{,}3.$$

b. From the data of VAN URK follows for argon:

$$\lambda\,(\text{per gr.}) = 58{,}06 - 0{,}2655\,T = 58{,}06\,(1 - 0{,}004573\,T),$$

which becomes with $T_k = 150{,}65$:

$$\lambda\,(\text{per gr. mol.}) = 58{,}06\,(1 - 0{,}689\,m) \times 39{,}95.$$

With $\gamma = 0{,}745$ we get $\gamma : (1+\gamma) = 0{,}427$, hence $\varepsilon' = \underline{1{,}61.}$
For μ may be written:

$$\mu = 2{,}02\,(145{,}44 - T) = 293{,}8\,(1 - 1{,}036\,m).$$

For $m = 0{,}5$ (about 75°, hence below the triple point at 84°) the equation becomes:

$$\left(\frac{\lambda'}{\mu'}\right)_{1/2} = \frac{38{,}06}{141{,}6} \times 39{,}95 : 2{,}021 = 5{,}31 = 5{,}3.$$

And for $m = 0$ we find:

$$\left(\frac{\lambda'}{\mu'}\right)_{0} = \frac{58{,}06}{293{,}8} \times 39{,}95 : 2{,}021 = 3{,}91 = 3{,}9.$$

c. For oxygen we find:

$$\lambda\,(\text{per gr.}) = 69.86 - 0{,}269\,T = 69{,}86\,(1 - 0{,}003856\,T),$$

which becomes with $T_k = 154{,}17$:

$$\lambda\,(\text{per gr.mol.}) = 69{,}86\,(1 - 0{,}595\,m) \times 16.$$

With $\gamma = 0{,}793$ $\gamma : (1+\gamma)$ becomes $= 0{,}442$, hence $\varepsilon' = \underline{1{,}35.}$
Further

$$\mu = 1{,}917\,(153{,}77 - T) = 294{,}8\,(1 - 1{,}003\,m).$$

Hence we have for $m = 0.5$:

$$\left(\frac{\lambda'}{\mu'}\right)_{1/2} = \frac{49{,}08}{147{,}0} \times 16 : 2{,}021 = 5{,}29 = 5{,}3.$$

And for $m = 0$:

$$\left(\frac{\lambda'}{\mu'}\right)_{0} = \frac{69{,}86}{294{,}8} \times 16 : 2{,}021 = 3{,}75.$$

d. For *nitrogen* we find:

$$\lambda\,(\text{per gr.}) = 72{,}20 - 0{,}3857\,T = 72{,}20\,(1 - 0{,}005342\,T),$$

or with $T_k = 125{,}96$:

$$\lambda\,(\text{per gr. mol.}) = 72{,}20\,(1 - 0{,}673\,m) \times 14{,}008.$$

With $\gamma = 0{,}813$ $\gamma : (1+\gamma)$ becomes $= 0{,}448$, so that $\varepsilon' = \underline{1{,}50.}$
We find for μ:

$$\mu = 2{,}002\,(124{,}29 - T) = 248{,}8\,(1 - 1{,}013\,m).$$

This yields for $m = 0{,}5$:

$$\left(\frac{\lambda'}{\mu'}\right)_{1/2} = \frac{47{,}90}{122{,}8} \times 14{,}01 : 2{,}021 = 5{,}40 = 5{,}4.$$

And with $m = 0$:

$$\left(\frac{\lambda'}{\mu'}\right)_0 = \frac{72{,}20}{248{,}8} \times 14{,}01 : 2{,}021 = 4{,}02 = 4{,}0.$$

e. In conclusion *hydrogen*. Here

$$\lambda \text{ (per gr.)} = 114{,}4 - 1{,}27\, T = 114{,}4\, (1 - 0{,}01110\, T).$$

With $T_k = 33{,}18$ this becomes:

$$\lambda \text{ (per gr. mol.)} = 114{,}4\, (1 - 0.3683\, m) \times 2{,}0154.$$

Further $\gamma_{th.} = 0{,}6$, hence $\gamma : (1 + \gamma) = 0{,}375$, through which ε' becomes $= \underline{0{,}98}$ (slight *decrease* of *a* when *t* becomes lower).

For μ is found:

$$\mu = 1{,}294\, (34{,}49 - T) = 44{,}63\, (1 - 0{,}962\, m).$$

For $m = 0{,}5$ we get therefore:

$$\left(\frac{\lambda'}{\mu'}\right)_{1/2} = \frac{93{,}34}{23{,}16} \times 2{,}0154 : 2{,}0212 = 4{,}02 = 4{,}0.$$

And with $m = 0$:

$$\left(\frac{\lambda'}{\mu'}\right)_0 = \frac{114{,}4}{44{,}63} \times 2{,}0154 : 2{,}0212 = 2{,}56 = 2{,}6.$$

And these values for benzene, argon etc. have been mentioned in § 4 for a comparison with the values, calculated from our formula for λ with f and f_0.

July 1925. *Tavel sur Clarens* (Suisse).

VI.

Appendix.

After I had written the foregoing paper, it has appeared to me that the quantity $x = l : u$ occurring in (1), which at the absolute zero (extrapolated) is about **5** for ordinary substances, 4 for argon etc., 3 for hydrogen, is $=$ **14** for all melted alkali-haloids. I shall discuss this more at length in a paper which will shortly appear in the Zeitschr. f. anorg. u. allg. Ch. (the third of a series of three papers on the substances mentioned [1])), and will give here only the principal results.

With $l : u = x$ the formula

$$\mu = \sigma\, v^{2/3} = \frac{1}{x}\, \frac{a}{v}\, \frac{1}{N^{1/3}}$$

follows, as we saw in § 1 (formula (1)), from $\sigma = \frac{a}{v^2}\, u$, since $l = (v : N)^{1/3}$. In this formula v is the molecular volume $M : D$. ($M =$ molecular weight, $D =$ density). As the quantity μ, i.e. the *molecular* surface-tension has an almost *linear* course from $T = 0$ to almost T_k (the difference between the point of intersection of this straight line with the temperature-axis and the real value of T_k is possibly about 10°, so that the error for the said salts will be about $10° : 3000° = {}^1/_{300}$), the coefficient of the temperature θ will be given with great approximation by

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[1] I in **146**, p. 263—280, II in **148**, p. 235—255, III in **149**, p. 324—352 (all in 1925).

$$\theta = \frac{\mu_0}{T_k} = \frac{1}{x_0} \frac{a_0}{v_0} \frac{1}{N^{1/3}} : \frac{8}{27} \lambda \frac{1}{R} \frac{a_k}{b_k} .$$

With $\lambda = \frac{27}{28}$, which is the value of this correction quantity in the formula for T_k for substances where γ is about $= 1$ (Zustandsgl. p. 140), θ becomes:

$$\theta = \frac{1}{x_0} \frac{7}{2} \frac{a_0}{a_k} \frac{b_k}{b_0} \frac{R}{N^{1/3}} ,$$

or with $R = 83{,}17 \,.\, 10^6$ (Ergs), $N = 0{,}6060 \,.\, 10^{24}$, hence $N^{1/3} = 0{,}8462 \,.\, 10^8 = 84{,}62 \,.\, 10^6$, so that $R : N^{1/3}$ becomes $= 1 : 1{,}0175$:

$$\text{(ordinary substances)} \quad \underline{\theta \mathrel{\overset{=}{>}} \frac{3{,}44}{x_0} \frac{a_0}{a_k} \frac{b_k}{b_0}} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (a)$$

With $x_0 > 5$, as we have found for ordinary substances, $a_0 : a_k = 1{,}6$ (Zust.gl. p. 250—255), $b_k : b_0 = 2\gamma =$ from 1,8 to 2, we therefore get for ordinary substances:

$$\theta = \frac{10{,}5}{x_0} = \underline{2{,}1} ,$$

2,1 being also found as mean value [1]).

But it follows from $x_0 = l_0 : u_0 = 5$, that $u_0 = l_0 : 5 = {}^2/_5\, r$, as for ordinary substances the radius of the molecule r will be about ${}^1/_2\, l$ for cubic distribution of the molecules. (For it is known that for these substances $(v - b) : v = m : f$, so that for $m = {}^1/_2\, (T = {}^1/_2\, T_k)$ the value $(v - b) : v$ is already $= {}^1/_2 : 7 = {}^1/_{14}$, hence $(l - r) : l = {}^1/_{42}$). For $T = 0$ the value r is strictly $= {}^1/_2\, l$.

Now it appears, however, that not only for ordinary substances, but also for the *melted alkalihaloids*

$$\underline{u_0 = {}^2/_5\, r} \, , \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (b)$$

in which now r is, however, much smaller than ${}^1/_2\, l$, as for ordinary substances. If $l_0 = 2\,r'$ is written, in which r' would therefore be the radius of the molecule if, as for ordinary substances, the elementary cubes are entirely filled with the molecule (thought spherical), (*a*) becomes quite generally:

$$\theta = 3{,}44 \frac{{}^2/_5\, r}{2r'} \frac{a_0}{a_k} \frac{b_k}{b_0} = 0{,}69 \frac{a_0}{a_k} \frac{b_k}{b_0} \frac{r}{r'} .$$

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[1]) For H_2 (with $x_0 = 2{,}8$, $a_0 : a_k = 0{,}9$, $b_k : b_0 = 1{,}2$) θ would become $= 1{,}3$, which again is in harmony with the value found.

The melted salts are all *electrolytically dissociated*. The values of μ used in practice are, however, calculated from the values determined experimentally by multiplication (see above) by $v^{2/3} = (M:D)^{2/3}$, in which the so-called "normal" value is taken for M, i.e. on the supposition that there is no electrolytic dissociation. (for KCl e.g. $= 74.6$). But (for total dissociation) this is, in fact, twice too great, as M should not have been taken for the whole molecule, but the mean value $^1/_2 M$ for each of the ions. In general M has been taken $(1+\alpha)$-times too great, hence μ and θ both $(1+\alpha)^{2/3}$-times too great. The above formula must, therefore, still be multiplied by $(1+\alpha)^{2/3}$ in order to find the "conventional" value of θ. (This is, therefore, found too great with dissociation, too small with association). In consequence of this we get quite generally:

$$\underline{\theta = 0{,}7 \frac{a_0}{a_k} \frac{b_k}{b_0} \frac{r}{r'} (1+\alpha)^{2/3}}, \quad . \; . \; . \; . \; . \; . \; . \quad (c)$$

and this for all cases where $u_0 = {}^2/_5\, r$. That the latter is also fulfilled with the melted alkalihaloids, as with the ordinary substances, follows from this that for the completely dissociated cesium salts $\underline{\theta = 0{,}8}$, so that, with $a_0 = a_k$ (as a has been found almost independent of the temperature for the great values of the valency attractions; cf. Zustandsgl. p. 325), $b_k : b_0 = 2\gamma = 1$ (as according to the third paper in the Z. f. anorg. Ch. cited the melted salts behave as boundary substances, where $\gamma = 1$) and $(1+\alpha)^{2/3} = 2^{2/3} = 1{,}59$, is found:

$$0{,}8 = 0{,}7 \times 1 \times 2 \times \frac{r}{r'} \times 1{,}6,$$

from which follows $r : r' = 0{,}8 : 2{,}2 = 1 : 2{,}75 = 1 : 2{,}8$. This latter (see below) has actually been found by LORENZ-BORN [1]), so that the supposition $u_0 = {}^2/_5\, r$ appears to be correct.

But then $x_0 = l_0 : u_0 = 2r' : {}^2/_5\, r = 5\,(r' : r)$ assumes also the value $5 \times 2{,}8 = \mathbf{14}$, as we already stated in the beginning. And this value is certainly very far from the "theoretic" value 4, which ought to be valid according to VAN URK (loc. cit.). We see clearly from all this, that in this and in allied problems a number of other factors play a part (as the values of $a_0 : a_k$, $b_k : b_0$, $r : r'$) than one would at first be inclined to suppose.

In passing we may just point out that in case of *association* (for ordinary substances) the factor $\left(\frac{1+\beta}{2}\right)^{2/3}$ must be substituted in (c) for $(1+\alpha)^{2/3}$, in which β is the degree of dissociation of the double molecules. Hence β is $= 0$ with complete association, so that then the value must be multiplied by $\left(\frac{1}{2}\right)^{2/3}$, i. e. *divided* by 1,6 — instead of multiplied, as with total electrolytic dissociation of the salt molecules.

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[1]) Cf. RICHARD LORENZ's excellent book: Raumerfüllung und Ionenbeweglichkeit, p. 242—257.

With melted electrolytes this electrolytic dissociation would increase the value of the (conventional) temperature coefficient θ, but in consequence of the fact that $a_0 : a_k = 1$ instead of 1,6, and particularly in consequence of the *very low* value of $r : r'$ (2,8 times less than for ordinary substances) θ is not found greater, but on the contrary *much smaller* than the normal value 2,1 holding for ordinary substances — which latter also ensues from (c) with $a_0 : a_k = 1{,}6$, $b_k : b_0 = 1{,}9$, $r : r' = 1$ and $\alpha = 0$.

That for the alkalihaloids really

$$\underline{r' : r = 2{,}8}\,, \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (d)$$

appears from what follows. The following values are e. g. calculated for $v_0 = M : D_0$ for the kations of the alkalihaloids (the values of D_0 have been calculated by me in the first paper in the Z. f. anorg. Ch. cited):

$$v_0 = \frac{6{,}94}{0{,}559} \quad \frac{23{,}00}{1{,}024} \quad \frac{39{,}10}{0{,}904} \quad \frac{85{,}45}{1{,}631} \quad \frac{132{,}8}{2{,}035},$$

or

$$v_0 = 12{,}41 \quad 22{,}24 \quad 43{,}25 \quad 52{,}39 \quad 65{,}26 \quad (\text{roughly } 1:2:4:5:6),$$

resp. for *Li*, *Na*, *K*, *Rb*. and *Cs*. Division by $N = 0{,}606 . 10^{24}$ yields, therefore, for the volume of the elementary cubes:

$$\omega = 20{,}48 \quad 36{,}70 \quad 71{,}37 \quad 86{,}45 \quad 107{,}7 . 10^{-14},$$

hence

$$l = \sqrt[3]{\omega} = 2{,}74 \quad 3{,}32 \quad 4{,}15 \quad 4{,}42 \quad 4{,}76 . 10^{-8},$$

or

$$r' = {}^1\!/_2\, l = 1{,}37 \quad 1{,}66 \quad 2{,}07 \quad 2{,}21 \quad 2{,}38 . 10^{-8}.$$

If now really $r' : r = 2{,}75$, the following values must be found for r: 0,498, 0,604, 0,755, 0,804, 0,865, i. e.

$$r = \mathbf{0{,}50} \quad \mathbf{0{,}60} \quad \mathbf{0{,}75} \quad \mathbf{0{,}80} \quad \mathbf{0{,}87} . 10^{-8},$$

while LORENZ-BORN (loc. cit.) found:

$$r = 0{,}45 \quad 0{,}51 \quad 0{,}69 \quad 0{,}77 \quad 0{,}83 . 10^{-8},$$

adding that these values are all somewhat too small. The conformity could not be better; particularly striking is the almost perfect identity of the value for *Na*, i. e. 0,604 found by us, with the value 0,605 calculated by LANDÉ (loc. cit. p. 251) from the quantum theory for the sodium atom.

If in (c) the values 0.55 (which is found as average value for the lithium haloids), 0,68 (*Na*-salts), 0,74 (id. *K*), 0,80 (id. *Rb*) and 0,82 (id. *Cs*), are substituted, it appears that resp.

$$(1 + \alpha)^{2/3} = 1{,}086 \quad 1{,}314 \quad 1{,}434 \quad 1{,}551 \quad 1{,}590,$$

hence

$$1 + \alpha = 1{,}13 \quad 1{,}51 \quad 1{,}72 \quad 1{,}93 \quad 2{,}00,$$

so that for the degree of dissociation α of the said salts resp. the values

$$\alpha = 0{,}13 \quad 0{,}51 \quad 0{,}72 \quad 0{,}93 \quad 1{,}00$$

are found.

Accordingly the melted *Li*-salts are dissociated only for about $^1/_8$, the sodium salts about half, the potassium salts for about $^3/_4$, and the rubidium and the cesium salts completely or almost completely.

By the discussion of the said relations for melted salts ($u_0 = {}^2/_5\, r$, $r' : r = 2{,}8$ etc.) and by the derivation of the general formula (c) for θ (about which so far nothing was known), I hope to have been of use to some scientists interested in this subject.

August 1925.

Chemistry. — *"An observation on the growth of crystals".* By P. TERPSTRA. (Communicated by Prof. F. M. JAEGER).

(Communicated at the meeting of September 26, 1925).

In his paper „Wachstum und Auflösung der Kristalle" J. J. P. VALETON[1]) discusses a. o. the following case: A very little crystal is placed in the centre of a spherical quantity of its slightly supersaturated solution. There is a device which cares that the concentration on the surface constantly remains C_2, whereas the concentration very near the growing crystal is C_1. Putting for the radius of the little crystal r_1, for the radius of the solution r_2, VALETON finds the concentration in any point:

$$C = -\frac{1}{r}\,\frac{r_1 r_2}{r_2 - r_1}(C_2 - C_1) + C_2 + \frac{r_1}{r_2 - r_1}(C_2 - C_1).$$

This question has its analogy in the discipline of electrostatics, viz. in the case of a spherical condenser. If the spheres have radii a and b and potentials V_a and V_b, the potential V in any point between the spheres appears to be:

$$V = -\frac{1}{r}\,\frac{ab}{b-a}(V_b - V_a) + V_b + \frac{a}{b-a}(V_b - V_a).$$

This analogy suffices to demonstrate that VALETON wrongly endeavours to deduce from his formula the so-called „Kristallisationshof-bildung". Just as in the case of the spherical condenser a „Hof" is out of the question, so in the case under discussion this phenomenon cannot appear in the neighbourhood of the growing crystal.

The formula for the velocity of crystal-growing which VALETON deduces from his theory is one of great value. A little crystal is supposed to be placed in a slightly supersaturated solution, which now, however, in contrast with the former case, is stirred thoroughly. Even then, it may be assumed that in the very neighbourhood of the crystal there is a layer of liquid with thickness s, which remains in a state of rest. At the surface of the crystal the solution has a concentration C_1, which is different at the different faces of the crystal, but is always a little more than the concentration of saturation C_0. The velocity of growing G of a face of the crystal can be put $k\ (C_1 - C_0)$, in which k is a constant which is characteristic for the crystal-face. Putting the concentration of the stirred solution C_2, VALETON deduces $G = R\,(C_2 - C_0)$. If the lines of diffusion are parallel to one another, as very approximately the case will be in points which lie opposite the middle-part of a crystal-face,

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[1]) Ztschr. f. Kryst. Bnd. **59**, 135; 335 Bnd. **60**, 1.

$$R = \frac{k\frac{D}{s}}{k+\frac{D}{s}} \quad (D = \text{the constant of diffusion of the solution}).$$

This formula shows very clearly that the velocity of growing of the various crystal-faces and in consequence their relative importance is not only a function of the crystal itself, as f. i. in the case of the property of cleavage: the properties of the solution also play a part.

To demonstrate in which manner the quantities k and $\frac{D}{s}$ produce the factor R of the observed velocity of growing, a graphical method may be applied which J. PLATEAU used in his work on two soap-bubbles in contact [1]. We are supposed to be given three right lines intersecting in the point M at angles of 60°. Now if we choose two points A and B so that $MA = k$ and $MB = \frac{D}{s}$, the line connecting the points A and B intersects the third line in a point C, so that $M\,C = R$. The figure illustrates that if one of the quantities k or $\frac{D}{s}$ is very great with respect to the other the value of R approaches to that of the latter. The crystal-faces which have their characteristic constant k greater than $M\,A$ have all a R value, which is between $M\,C$ and $M\,D$ $(M\,D = M\,B)$. So there is a possibility that while the characteristic constants k are very different, yet the observed velocities of growing differ but little, so that they may cause the formation of convex-curved parts in the surface of the crystal. In most cases, however, these curved parts have no chance to develop, because they are effaced by the faces which grow slowly. In this connection one might think of some cases among the minerals and of the explosive cubes which grow from a satured solution of ammonium-chloride, to which had been added a little quantity of $Cd\,Cl_2$. These cubes, which are rather strongly endowed with the property of double refraction, have planes which are very obviously curved.

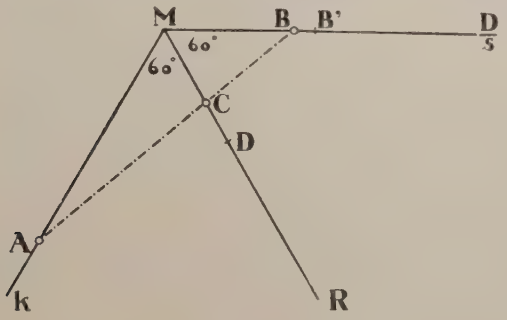

Fig. 1.

In the neighbourhood of the margins of a crystal-face the lines of diffusion form a convergent system of lines. The formula of the velocity of growing takes the form:

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[1] J. PLATEAU: *Statique expérimentale et théorique des liquides* (1873) Vol. I pag. 299.

$$G = \frac{k \, . \, \varepsilon \, . \, \frac{D}{s}}{k + \varepsilon \frac{D}{s}} (C_2 - C_0) \text{ in which } \varepsilon > 1.$$

This means that in the figure with the margin of a crystal-face a point B' corresponds, that lies a little farther to the right than B, so that the line AB' cuts the third line in a point C'. MC' being slightly greater than MC, the diagram shows that in the case of a crystal that grows in a throughly stirred solution, there may be on the margins of a crystal-face a velocity of growing which is slightly greater than that velocity of the central part of that face. This increase of the velocity of growing will be relative small if k is small relative to $\frac{D}{s}$, whereas $\frac{MC'}{MC}$ approaches to $\varepsilon \left(= \frac{MB'}{MB} \right)$ if k becomes great relative to $\frac{D}{s}$ (cf. Fig. 2).

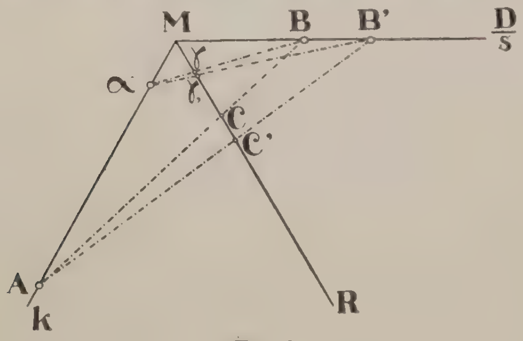

Fig. 2.

Notwithstanding the above mentioned effect, the faces which are growing slowly have, therefore, the greater chance to remain plane to the margin.

Mathematics. — "*On treating Skew Correlation*". By Prof. M. J. VAN UVEN. (Communicated by Prof. W. KAPTEIJN).

(Communicated at the meeting of September 26, 1925).

Biological Statistics — founded by QUETELET and GALTON — deal with sets of similar individuals (for instance: adult men of the same race, trees of the same kind in the same wood). In whatever point the individuals of such a set may agree with another, yet they are not quite equal; for instance: all the trees of the same kind in the same wood are not equally thick. Nevertheless the similitude of the individuals of such a set is typified i.a. by the fact that the amount of such a measurable characteristic (length of body, thickness of the trunk) varies comparatively little among the individuals, at least so little that it is reasonable to speak of a typical value, a standard value, round which the amounts, found in the different individuals, oscillate.

The quantity the amount of which is measured in the different individuals being denoted by x, and the concrete values observed in determinate individuals being expressed by $\xi_1, \xi_2, \ldots \xi_n$, these ξ_k are partly larger, partly smaller than a certain standard value X, whence the deviations $v_k = \xi_k - X$ turn out to be partly positive, partly negative.

The total number N of individuals being large, the determinate value ξ_k will appear more than once, say Y_k times. This number Y_k is called the *frequency* of ξ_k. Evidently $\sum_{k=1}^{n} Y_k = N$.

As a rule the frequency Y_k of ξ_k is stated to be larger according as ξ_k differs less from the standard value X, that is to say: according as the absolute value of v_k be less, so that Y_k and ξ_k seem to be functionnally related to each other. In a good many cases this relation is stated to be satisfactorily expressed by the GAUSSian exponential law of error, viz: Being chosen as standard value the arithmetical mean $\bar{\xi} = \dfrac{\sum_{1}^{n} Y_k \xi_k}{N}$ of the observed values ξ_k, and being formed the differences $u_k = \xi_k - \bar{\xi}$, the deviations from that mean, then the frequency Y_k is proportional to $e^{-h^2 u^2_k}$, where h is a constant, the so-called "modulus of precision", which is connected with the "mean error" $\varepsilon = \sqrt{\overline{u^2}} = \sqrt{\dfrac{\Sigma Y_k u_k^2}{N}}$ by the well-known relation $h \varepsilon \sqrt{2} = 1$.

The exponentional law, more precisely expressed, runs:

The probability W_a^b, that x is found between a and b, is

$$W_a^b = \frac{h}{\sqrt{\pi}} \int_a^b e^{-h^2(x-\overline{\xi})^2}\, dx.$$

In this expression there appear besides the limits a and b two independent constants, viz. $\overline{\xi}$ and h. So, to construct the law of error, which is supposed to agree with a given frequency series, these two constants are to be derived from the given quantities ξ_k, Y_k $(k=1,2\ldots n)$ by means of the relations

$$\overline{\xi} = \frac{\sum_1^n Y_k\, \xi_k}{N}, \quad h = \frac{1}{\varepsilon\sqrt{2}}, \quad \varepsilon^2 = \overline{u^2} = \frac{\sum_1^n Y_k\, u_k^2}{N} = \frac{\sum_1^n Y_k\, (\xi_k - \overline{\xi})^2}{N}.$$

Usually the observed ξ_k form an arithmetic progression. The successive values being $\xi_1, \xi_2 \ldots \xi_n$, then

$$\xi_{k+1} - \xi_k = c;$$

c is called the class-interval.

The values ξ_k often being obtained by estimation, and accordingly being rounded results of measuring, the frequency Y_k really expresses that it is stated Y_k times that x is found between $\xi_k - \frac{c}{2}$ and $\xi_k + \frac{c}{2}$, whence the theoretical probability of ξ_k amounts to

$$W_k = \frac{h}{\sqrt{\pi}} \int_{\xi_k - \frac{c}{2}}^{\xi_k + \frac{c}{2}} e^{-h^2(x-\overline{\xi})^2}\, dx. \quad \ldots\ldots\ldots \quad (1)$$

For the given frequency series to agree exactly with this exponential law of error, the relation

$$W_k = \frac{Y_k}{N}$$

must appear to hold good.

Thus by comparing the empirical values of the quotients $\frac{Y_k}{N} = y_k$ (relative frequencies) with the theoretical values W_k, we can examine whether the given frequency series really agrees or not with the "normal" law of frequency.

We are also able to experiment further on this agreement by tests which are the more valuable as they embrace the whole material of observations. They are founded on the following considerations:

1°. Theoretically the mean absolute value of u, viz. $\overline{|u|} = \eta$ must equal $\sqrt{\frac{2}{\pi}} \times \varepsilon$; thus $\eta_{\text{theor.}} = \sqrt{\frac{2}{\pi}} \cdot \varepsilon = 0.79788\ldots \varepsilon$.

2^0. Theoretically the mean third power of u must be zero, or $\overline{u^3}=0$.

3^0. Theoretically the mean fourth power of u must equal $3\varepsilon^4$, in other words: $\overline{u^4}=3\varepsilon^4$.

In order to become independent from the unit, in which x (and so $u=x-\xi$, and ε) is expressed, we form the expressions

$$S=\frac{\overline{u^3}}{\varepsilon^3} \text{ and } E=\frac{\overline{u^4}}{\varepsilon^4}-3,$$

resp. called Skewness and Excess.

Now, for the empirical value of η : $\eta_{\text{emp.}}=\frac{\Sigma Y_k \mid u_k \mid}{N}$ there being found a value little different from $\sqrt{\frac{2}{\pi}}\,.\,\varepsilon$ and for $S_{\text{emp.}}=\frac{\Sigma Y_k u_k{}^3}{N\varepsilon^3}$ and $E_{\text{emp.}}=\frac{\Sigma Y_k u_k{}^4}{N\varepsilon^4}-3$ very small numbers, these statements suggest the idea that the given frequency distribution substantially answers to the normal (exponential) law of frequency, and that the remaining small discrepancies between y_k and W_k may be imputed to accidental perturbations.

In the theory of correlation each individual of a statistical manifoldness is considered with regard to two or more measurable characteristics: $x, x', x'', \ldots$; for instance: among adult men of the same race: length of body, circumference of the chest, eye distance, . . .; among trees of the same kind in the same wood: thickness of the trunk, height, volume of the trunk, . . .

Arranging the observed values of x according to ascending magnitude $\xi_1, \xi_2 \ldots \xi_n$ (where usually $\xi_{k+1}-\xi_k=c$ is constant), and, equally, the observed values of x': $\xi'_1, \xi'_2 \ldots \xi'_n$ (where, as a rule, $\xi'_{l+1}-\xi_l=c'$), and so on with regard to the other variables, each individual of the manifoldness will then furnish a set $\xi_k, \xi'_l, \xi''_m, \ldots$ The number N of the individuals being very large, such a set of concrete measured values will occur more than once, say $Y_{klm\ldots}$ times. We shoud then establish a functional relation between $Y_{klm\ldots}$ on one hand and $\xi_k, \xi'_l, \xi''_m, \ldots$ on the other.

By expanding the GAUSSian exponential law of error to more than one variable, BRAVAIS [1]) established a chance formula, according to which the probability $W_{klm\ldots}$ of the set $\xi_k, \xi'_l, \xi''_m, \ldots$ is proportional to $e^{-f(u_k, u'_l, u''_m, \ldots)}$, where $f(u, u', u'', \ldots) \equiv A\,u^2+B\,uu'+C\,u'^2+D\,u\,u''+E\,u'u''+F\,u''^2+\ldots$ is a positive definite homogeneous quadratic function of the variables

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[1]) A. BRAVAIS. ,,Analyse mathématique sur les probabilités des erreurs de situation d'un point''. Paris: Mémoires présentés par divers savants à l'Académie royale des sciences de l'Institut de France; T. 9 (1846) p. 255.

$u = \xi - \overline{\xi}$, $u' = \xi' - \overline{\xi'}$, $u'' = \xi'' - \overline{\xi''}$, ... If the coefficients B, D, E, ... of the products uu', uu'', $u'u''$, ... are different from zero, we may then conclude that the probability of a certain u, say u', depends on the accompanying u, u''...; so the quantities $x, x'\ x''$... mutually affect their values, or, in other words, the quantities x, x', x''... cannot vary independently from each other, or, again: there exists a mutual connection, a "correlation" between them.

Thus: among the trees of the same kind in the same wood, the highest will, in the main, also be the thickest and have the largest volume of trunk.

In the present paper we shall exclusively confine ourselves to two variables, x and x'. In this case the chance formula runs:

$$W_{kl} = \frac{h\,h'\sqrt{1-\gamma^2}}{\pi} \int\limits_{x=\xi_k-\frac{c}{2},}^{\xi_k+\frac{c}{2}} \int\limits_{x'=\xi'_l-\frac{c'}{2}}^{\xi'_l+\frac{c'}{2}} e^{-(h^2u^2 - 2\gamma h\,h' u\,u' + h'^2 u'^2)}\, du\, du' \quad . \quad . \quad . \quad (2)$$

Taking a determinate value of u', say u'_λ, the average concurring quantity u appears to be $(\overline{u})_\lambda = \gamma \frac{h'}{h} u'_\lambda$. So this average value is proportional to u'_λ, whence $(\xi)_\lambda - \overline{\xi} = \gamma \frac{h'}{h} (\xi'_\lambda - \overline{\xi'})$, that is to say: $(\xi)_\lambda$ is a linear function of ξ'_λ. On account of this property in the above case the connection is called: linear correlation.

Being $u_k = \xi_k, - \overline{\xi}$, $u' = \xi'_l - \overline{\xi'}$, the probability formula (2) contains, besides the class-intervals c and c', which occur in the limits, five constants, viz. the two averages $\overline{\xi}, \overline{\xi'}$, the two "moduli" h, h' and the so-called coefficient of correlation γ, the last having always its absolute value ≤ 1.

If $\gamma > 0$ the correlation is said to be positive, if $\gamma < 0$ to be negative. Now from (2) follows

$$\mu = \varepsilon^2 = \overline{u^2} = \frac{1}{2h^2(1-\gamma^2)}, \quad \mu' = \varepsilon'^2 = \overline{u'^2} = \frac{1}{2h'^2(1-\gamma^2)}, \quad \lambda = \overline{u\,u'} = \frac{\gamma}{2h\,h'(1-\gamma^2)}.$$

Hence the five constants mentioned above may be found empirically from

$$\overline{\xi} = \frac{\Sigma Y_{kl}\xi_k}{N}, \quad \overline{\xi'} = \frac{\Sigma Y_{kl}\xi'_l}{N}, \quad \mu = \frac{\Sigma Y_{kl}u_k^2}{N}, \quad \mu' = \frac{\Sigma Y_{kl}u'^2_l}{N}, \quad \lambda = \frac{\Sigma Y_{kl}u_k\,u'_l}{N},$$

where the sums are taken over k from 1 to n, over l from 1 to n'.

In order to control whether a given two-dimensional frequency scheme ξ_k, ξ'_l, Y_{kl} agrees satisfactorily with the formula (2) or not, we might make some tests, e.g. by making use of the following theoretical relations:

$$\overline{u^3} = 0, \quad \overline{u^2 u'} = 0, \quad \overline{u\,u'^2} = 0, \quad \overline{u'^3} = 0;$$

$$\overline{u^4} = 3\varepsilon^4, \quad \overline{u^3u'} = 3\gamma\,\varepsilon^3\varepsilon', \quad \overline{u^2u'^2} = (1+2\gamma^2)\,\varepsilon^2\varepsilon'^2, \quad \overline{uu'^3} = 3\gamma\varepsilon\varepsilon'^3, \quad \overline{u'^4} = 3\varepsilon'^4,$$

where, as above, the notation $\overline{f(u, u')}$ always expresses the average value of $f(u, u')$, so that its empirical value is

$$\{\overline{f(u, u')}\}_{\text{emp.}} = \frac{\Sigma Y_{kl} f(u_k, u'_l)}{N} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Desiring to get rid of the influence of the units of x and x' (so of u and u' and of ε and ε'), it is preferable to construct the following expressions, which are analogous to the Skewness and the Excess in the case of one variable:

$$S = \frac{\overline{u^3}}{\varepsilon^3}, \qquad S'_1 = \frac{\overline{u^2 u'}}{\varepsilon^2 \varepsilon'}, \qquad S_1 = \frac{\overline{u u'^2}}{\varepsilon \varepsilon'^2}, \qquad S' = \frac{\overline{u'^3}}{\varepsilon'^3},$$

$$E = \frac{\overline{u^4}}{\varepsilon^4} - 3,\ E'_1 = \frac{\overline{u^3 u'}}{\varepsilon^3 \varepsilon'} - 3\gamma,\ E_2 = \frac{\overline{u^2 u'^2}}{\varepsilon^2 \varepsilon'^2} - 1 - 2\gamma^2,\ E_1 = \frac{\overline{u u'^3}}{\varepsilon \varepsilon'^3} - 3\gamma,\ E' = \frac{\overline{u'^4}}{\varepsilon'^4} - 3.$$

All these expressions are theoretically equal to zero.

If their empirical values are very small, one may be convinced that the given frequency scheme — apart from accidental perturbations — corresponds to the two-dimensional exponential chance formula (2).

We now return for a moment to the frequency distribution with only one variable.

However often the frequency distribution offered by practice may even be represented by the normal law of distribution, yet it often happens that a given frequency distribution shows deviations from the normal law of distribution too striking and too systematic to be considered a normal distribution accidentally disturbed. On drawing a diagram of such a frequency distribution by plotting an ordinate Y_k above each point ξ_k of the x-axis, it is impossible to draw a normal frequency curve through the points thus obtained, but a skew frequency curve can be drawn.

The investigation of skew frequency curves has already been carried on on all sides. Besides the work of the Biometric school of KARL PEARSON, which aims at deducing a set of formulae giving account numerically for the frequency distributions occurring in practice, no attempts have been wanting to explain the origin of skew frequency distributions. A start has usually been made from the GAUSSian normal law of error. Several — among others the Danish astromer T. N. THIELE [1]), the Swedish astronomer C. V. L. CHARLIER [2]) and the English statistician F. Y. EDGEWORTH [3]), are especially worth mentioning — in deducing a more general law of error have attached themselves to the methods of LAPLACE and POISSON, broadening the basis of their theory. So the formula

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[1]) T. N. THIELE. Theory of observations. London 1903. Ch. & E. Layton.

[2]) C. V. L. CHARLIER. Ueber das Fehlergesetz. Arkiv för Matem., Astr., och Fysik Bd. N⁰. 8 (1905). Researches into the theory of Probability. Lunds Univ. Årsskrift. N.F. Afd. 2, Bd. 1 N⁰. 5, Lund 1906.

[3]) F. Y. EDGEWORTH. The Law of Error. Transactions of the Cambridge Phil. Soc. Vol. XX (1908), pp. 36 and 113.

$$e^{-h^2u^2}(A + Bu^3 + Cu^4 + \ldots)$$

is established, which is derived by several authors, and is called by CHARLIER: the law of frequency type A. CHARLIER [1]) too has deduced quite a different formula (law of frequency type B) starting from the POISSON law of distribution.

It is, however, possible to start from another point of view. Both the above mathematician EDGEWORTH [2]) and the Dutch astronomer J. C. KAPTEYN [3]) have pointed to the possibility that the normal law of frequency may be maintained in the most general case, provided it be granted, that the quantity which is normally distributed is not necessarily the directly observed quantity x, but rather a function $f(x)$ of this quantity. EDGEWORTH admitted that this function answers to the form $f(x) = A + Bx + Cx^2$. On the other hand KAPTEYN, in his first publication: „Skew Frequency Curves in Biology and Statistics", has adopted the form $f(x) = (x + \varkappa)^q$. The special merits of KAPTEYN are — in my opinion — that he derived the normal distribution of a function of x from very simple suppositions concerning the growth conditions of the x directly observed, viz. by admitting that the elementary increment of x depends on the value already reached.

While both EDGEWORTH and KAPTEYN, in tracing the function $f(x)$ which is really distributed normally, have confined themselves to a concrete type of function, the present writer [4]) has tried, in the 2nd part of KAPTEYN's "Skew Frequency Curves", to determine this function without any premised supposition with regard to its analytic structure. It was only necessary — in order to make the problem determinate — to introduce some simplifying suppositions upon finiteness, continuity, etc. By modifying some of these suppositions it moreover appeared to be possible to account for particular irregularities in several frequency distributions [5]).

Since the method of treating skew correlation (i. e. non-normal frequency schemes of two, or more, variables) suggested in the following paper will depend on the method of analysing skew frequency curves, last mentioned, this method will be sketched here in its principal outlines, referring the reader for further details to the original paper.

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[1]) C. V. L. CHARLIER: Die zweite Form des Fehlergesetzes. Arkiv för Matem., Astron., och Fysik. Bd. 2 N⁰. 15 (1905). Researches (see above).

[2]) F. Y. EDGEWORTH: On the Representation of Statistics by Mathematical Formulae. Journal of the R. Statistical Society. Vol. 61 (1898) p. 670, Vol. 62 (1899) p. 125, p. 373 and p. 534, Vol. 63 (1900) p. 72.

[3]) J. C. KAPTEYN. Skew Frequency Curves in Biology and Statistics. Groningen, 1903, Noordhoff.

[4]) J. C. KAPTEYN and M. J. VAN UVEN: Skew Frequency Curves in Biology and Statistics. 2nd Paper. Groningen, 1916, Noordhoff.

[5]) M. J. VAN UVEN. Skew Frequency Curves. These Proceedings 19, p. 670.

Given the frequency scheme ξ_k, Y_k $(\sum\limits_{1}^{n} Y_k = N)$, the meaning is, that Y_k values of x lie between $\xi_k - \frac{c}{2}$ and $\xi_k + \frac{c}{2}$, or, putting

$$\xi_k + \frac{c}{2} = x_k \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

between x_{k-1} and x_k.

So, with $Y_1 + Y_2 + \ldots + Y_k = \sum\limits_{i=1}^{k} Y_i$ individuals x lies beneath x_k. The theoretical lower limit x_0 ought not to be equal to $\xi_1 - \frac{c}{2}$, but may be smaller, since the theoretical frequencies may sink beneath the empirical minimum value 1. For the same reason the theoretical upper limit x_n may surpass $\xi_n + \frac{c}{2}$.

We next consider a function $z = f(x)$ normally distributed round the mean 0 and unimodular (i. e. with $h = 1$), and require that the corresponding intervals $x_0 \rightarrow x_k$ and $z_0 = f(x_0) \rightarrow z_k = f(x_k)$ be equally probable.

Besides, we admit — as a simplifying supposition — that the (unimodular) variable z is a continuous, univalent, ever increasing function of x. Then z_0 is the theoretical lower limit of the variable z normally distributed, thus $z_0 = -\infty$; likewise we have $z_n = +\infty$. So the z_k conjugate to x_k is determined by

$$p_k = \frac{Y_1 + Y_2 + \ldots + Y_k}{N} = \frac{\sum\limits_{i=1}^{k} Y_i}{N} = \frac{1}{\sqrt{\pi}} \int\limits_{-\infty}^{z_k} e^{-z^2} \, dz = \Theta(z_k) \quad . \quad . \quad (5)$$

The values x_0 and x_n, conjugate to $z_0 = -\infty$ and $z_n = +\infty$ being indeterminate, we obtain $n-1$ equations $p_k = \Theta(z_k)$ $(k=1, 2 \ldots n-1)$, thus $n-1$ pairs (x_1, z_1), $(x_2, z_2) \ldots (x_{n-1}, z_{n-1})$. So $n-1$ values of the function $z = f(x)$ are known.

Representing the pairs (x, z) by the coordinates x, z, the problem, translated into geometrical language, runs: to draw a (curve) line through $n-1$ points.

Hence the problem proposed is indeterminate in a high degree. Nevertheless it is possible in a good many cases to draw a simple line (corresponding to a simple function $z = f(x)$) through these points.

Then the analytical expression of the curve is a suitable solution of the function required. In choosing $f(x)$ we also have particularly in mind the obtaining of a simple form for the so-called "reaction function" $\eta = 1 : \frac{d\,f(x)}{dx}$. If, in particular, the $n-1$ points lie in a straight line, we may conclude from it that the given frequency distribution is a normal one. So this method furnishes a criterion for the being normal of a frequency distribution.

Likewise the frequency scheme of a set of two variables often shows deviations from the ideal distribution (according to (2)) so striking, that these deviations cannot reasonably be imputed to accidental perturbations of a linear correlation scheme.

On drawing a spatial diagram of such a non-normal two-dimensional frequency distribution by plotting above each point (ξ_k, ξ'_l) of the (x, x')-plane a third coordinate Y_{kl}, it is impossible to lay a normal frequency surface through these points, but a "skew surface" can be put.

The spine of the normal frequency surface having a rectilinear projection on the (x, x')-plane, the spine of such a skew frequency surface has a curvilinear projection on the (x, x')-plane. In this case the squares of the frequency table which contain the highest frequencies, lie in a curved row; hence we introduce the denomination "*skew* correlation".

Investigations on skew correlation are comparatively rare. An important one is due to N. R. JØRGENSEN[1], who in his paper „Undersøgelser over Frequensflader of Korrelation", treats correlation of two variables, making use of CHARLIER's two types A and B.

The aim of this paper is to analyse skew correlation of two variables, x and x' according to the principle of EDGEWORTH-KAPTEYN, by reducing it to a linear correlation between two functions t and t', which in general may depend on both x and x'.

As we have already pointed out, we shall make use of the method, which in the case of one variable has given us an idea of the function $z = f(x)$ normally spread.

We may formulate the data in this way:

Both quantities x and x' are observed with each of N individuals. For x are found n ascending values: $\xi_1, \xi_2, \ldots \xi_k \ldots \xi_n$, for x' n' ascending values: $\xi'_1, \xi'_2, \ldots \ldots \xi'_l, \ldots \xi'_{n'}$. The combination

x' x	ξ'_1	ξ'_2		ξ'_l			$\xi'_{n'}$
ξ_1	Y_{11}	Y_{12}		Y_{1l}			$Y_{1n'}$
ξ_2	Y_{21}	Y_{22}		Y_{2l}			$Y_{2n'}$
ξ_k	Y_{k1}	Y_{k2}		Y_{kl}			$Y_{kn'}$
ξ_n	Y_{n1}	Y_{n2}		Y_{nl}			$Y_{nn'}$

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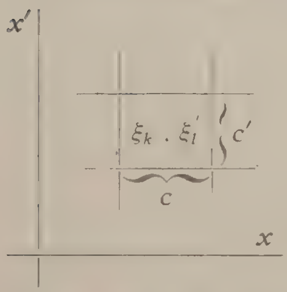
[1] N. R. JØRGENSEN. Undersøgelser over Frequensflader og Korrelation. København, 1916. Arn. Busck.

ξ_k, ξ'_l is stated Y_{kl} times. These frequencies are clearly summarized by the frequency scheme; of the variable x the ascending values are tabulated downwards, of the variable x' the ascending values run to the right.

Usually the values $\xi_1, \xi_2, \ldots \xi_k \ldots \xi_n$ increase by the same interval c (so that $\xi_{k+1} = \xi_k + c$), the values $\xi'_1, \xi'_2, \ldots \xi' \ldots \xi'_{n'}$, by the same interval c' (so that $\xi'_{l+1} = \xi'_l + c'$).

By denoting the rounded numbers ξ_k, ξ'_l we really mean that x is found between $\xi_k - \frac{c}{2}$ and $\xi_k + \frac{c}{2}$, and that x' lies between $\xi'_l - \frac{c'}{2}$ and $\xi'_l + \frac{c'}{2}$.

So, representing x and x' by rectangular coordinates, the combination (ξ_k, ξ'_l) indicates, that the "point" (x, x') lies within a rectangle the sides of which are $x = \xi_k - \frac{c}{2}$, $x = \xi_k + \frac{c}{2}$, $x' = \xi'_l - \frac{c'}{2}$ and $x' = \xi'_l + \frac{c'}{2}$. Hence Y_{kl} points (x, x') are found within this rectangle. Only this proposition must be less positive at the extreme limits.



If $D(x, x')$ be the theoretical probability function, so that the chance that the point (x, x') lies within the infinitesimal domain $(\xi, \xi + dx, \xi', \xi' + dx')$ is

$$dW = D(\xi, \xi')\, dx\, dx',$$

then we have for the frequency Y_{kl} corresponding to the probability

$$y_{kl} = \frac{Y_{kl}}{N}$$

$$Y_{kl} = N \,.\, y_{kl} = N \,.\int_{x=\xi_k-\frac{c}{2}}^{x=\xi_k+\frac{c}{2}} \int_{x'=\xi'_l-\frac{c'}{2}}^{x'=\xi'_l+\frac{c'}{2}} D(x, x') \,.\, dx \,.\, dx' = N \int_{x=\xi_k-\frac{c}{2}}^{x=\xi_k+\frac{c}{2}} \int_{x'=\xi'_l-\frac{c'}{2}}^{x'=\xi'_l+\frac{c'}{2}} dW \;. \quad (6)$$

We have now to bring the probability function $D(x, x')$ into a form, which corresponds to a positive linear correlation between two unimodular functions $t(x, x')$ and $t'(x, x')$; that is to say; to determine two functions t and t' in such a way that

$$D(x\, x') = \frac{\sqrt{1-\gamma^2}}{\pi} e^{-(t^2 - 2\gamma t t' + t'^2)} \frac{\partial(t, t')}{\partial(x, x')} \quad . \; . \; . \; . \; . \quad (7)$$

being

$$\frac{\partial(t, t')}{\partial(x, x')} = \begin{vmatrix} \frac{\partial t}{\partial x}, & \frac{\partial t'}{\partial x} \\ \frac{\partial t}{\partial x'}, & \frac{\partial t'}{\partial x'} \end{vmatrix}$$

and γ the coefficient of correlation $(0 \leqq \gamma \leqq 1)$.

It is easy to understand, and, moreover, it will appear from the following reasoning that the problem, put in full generality, is indeterminate.

We can therefore only succeed in solving it by introducing limiting (if possible simplifying) conditions.

We shall next transform the infinitesimal probability

$$dW = \frac{\sqrt{1-\gamma^2}}{\pi}\, e^{-(t^2-2\gamma t t'+t'^2)} \frac{\partial\,(t,\,t')}{\partial(x,x')} \,.\, dx \,.\, dx' \rightarrow \frac{\sqrt{1-\gamma^2}}{\pi}\, e^{-(t^2-2\gamma t t'+t'^2)}\, dt \,.\, dt'$$

into a canonic form. This may be done in several ways:

1°. Putting

$$\sqrt{1-\gamma^2}\,.\,t = z \quad , \quad t' - \gamma t = \zeta,$$

so that

$$\frac{\partial\,(t,\,t')}{\partial\,(z,\,\zeta)} = \frac{1}{\sqrt{1-\gamma^2}},$$

we find

$$dW = \frac{1}{\pi} e^{-(z^2+\zeta^2)}\; dz \,.\, d\zeta = \frac{e^{-z^2}}{\sqrt{\pi}}\, dz \,.\, \frac{e^{-\zeta^2}}{\sqrt{\pi}}\, d\zeta,$$

or, introducing

$$\frac{1}{\sqrt{\pi}} \int_{-\infty}^{z} e^{-v^2}\, dv = \Theta\,(z) = s, \qquad \frac{1}{\sqrt{\pi}} \int_{-\infty}^{\zeta} e^{-v^2}\, dv = \Theta\,(\zeta) = \sigma \quad . \quad . \quad (8)$$

$$dW = ds \,.\, d\sigma \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (I)$$

2°. Putting

$$\sqrt{1-\gamma^2}\,.\,t' = z' \quad , \quad t - \gamma\, t' = \zeta',$$

we obtain

$$dW = \frac{1}{\pi} e^{-(z'^2+\zeta'^2)}\; dz' \,.\, d\zeta' = \frac{e^{-z'^2}}{\sqrt{\pi}}\, dz' \,.\, \frac{e^{-\zeta'^2}}{\sqrt{\pi}}\, d\zeta',$$

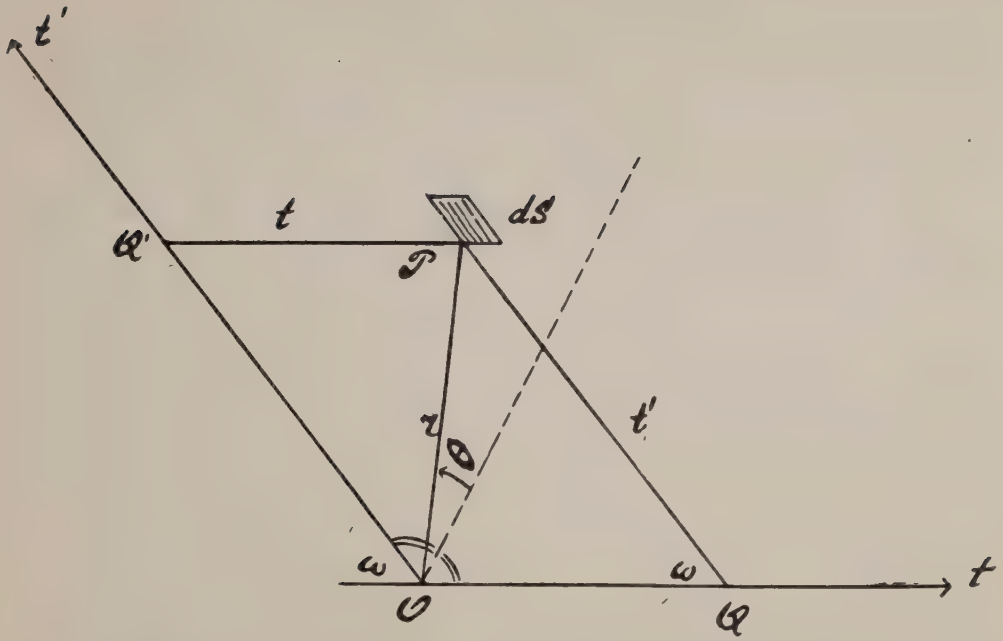
or, introducing

$$\frac{1}{\sqrt{\pi}} \int_{-\infty}^{z'} e^{-v^2}\, dv = \Theta\,(z') = s', \qquad \frac{1}{\sqrt{\pi}} \int_{-\infty}^{\zeta'} e^{-v^2}\, dv = \Theta\,(\zeta') = \sigma',$$

$$dW = ds' \,.\, d\sigma' \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (II)$$

3. A third manner suggests itself by introducing t and t' as non-rectangular coordinates, the positive axes of which include an angle $\pi-\omega$, ω being given by

$$\cos\omega = \gamma.$$



Denoting the radius vector OP of the point (t, t') by r, we have

$$r^2 = t^2 - 2\cos\omega \,.\, t t' + t'^2 = t^2 - 2\gamma\, t t' + t'^2.$$

The element of area dS, i. e. the elementary parallelogram on dt, dt', with included angle $\pi - \omega$, is found to be

$$dS = dt \,.\, dt' \,.\, \sin(\pi - \omega) = \sin\omega \,.\, dt \,.\, dt' = \sqrt{1-\gamma^2} \,.\, dt \,.\, dt'\,;$$

whence

$$dW = \frac{e^{-r^2}}{\pi}\, dS.$$

We next pass on to polar coordinates. The polar axis of the argument θ may coincide with the bisector of the positive axes (t) and (t').

Then from

$$\angle POQ = \theta + \frac{\pi - \omega}{2} = \frac{\pi}{2} - \left(\frac{\omega}{2} - \theta\right),$$

$$\angle OPQ = \pi - \omega - \angle POQ = \frac{\pi}{2} - \left(\frac{\omega}{2} + \theta\right),$$

results

$$\frac{t}{\cos\left(\dfrac{\omega}{2} + \theta\right)} = \frac{t'}{\cos\left(\dfrac{\omega}{2} - \theta\right)} = \frac{r}{\sin\omega}$$

or

$$t = \frac{r}{\sin\omega}\cos\left(\frac{\omega}{2} + \theta\right), \qquad t' = \frac{r}{\sin\omega}\cos\left(\frac{\omega}{2} - \theta\right).$$

Inversely from

$$t'-t=\frac{2r}{\sin\omega}\sin\frac{\omega}{2}\sin\theta=\frac{r\sin\theta}{\cos\frac{\omega}{2}}\quad\text{and}\quad t'+t=\frac{2r}{\sin\omega}\cos\frac{\omega}{2}\cos\theta=\frac{r\cos\theta}{\sin\frac{\omega}{2}}$$

we derive

$$\operatorname{tg}\theta=\frac{t'-t}{t'+t}\cot\frac{\omega}{2}=\frac{t'-t}{t'+t}\sqrt{\frac{1+\gamma}{1-\gamma}},$$

r being found from

$$r^2=t^2-2\gamma\, t\, t'+t'^2.$$

At present the element of area comes out at

$$dS=r\,.\,dr\,.\,d\theta,$$

whence

$$dW=\frac{e^{-r^2}}{\pi}\,r\,.\,dr\,.\,d\theta,$$

or, putting

$$2\int_0^r e^{-v^2}\,v\,dv=1-e^{-r^2}=\varphi\quad,\quad\frac{\theta}{2\pi}=\psi,$$

$$dW=d\varphi\,.\,d\psi\qquad\ldots\ldots\ldots\ldots\qquad(III)$$

So we have separated the two-dimensional differential dW in three different ways into a product of two one-dimensional differentials.

These three products not being equal to each other, the three differentials dW are no more equal. Yet each of them may be used as two-dimensional element of the chance W.

We meet the same state of things in expressing the element of area in different systems of coordinates. x, x' being a system of rectangular coordinates, r, θ a system of polar coordinates, we may note for the areal increment both $dx\,.\,dx'$ and $r\,.\,dr\,.\,d\theta$, without being $dx\,.\,dx'=r\,.\,dr\,.\,d\theta$.

We shall indicate this equivalency in representing the two-dimensional differential in a double integral by $\rightleftarrows$. Thus $dx\,.\,dx'\rightleftarrows r\,.\,dr\,.\,d\theta$. The meaning of the latter is therefore

$$\frac{\partial\,(x, x')}{\partial\,(r\,.\,\theta)}=r.$$

So, from

$$dW=D\,(x, x')\,.\,dx\,.\,dx'\rightleftarrows ds\,.\,d\sigma\rightleftarrows ds'\,.\,d\sigma'\rightleftarrows d\varphi\,.\,d\psi$$

may be concluded

$$D\,(x, x')=\frac{\partial\,(s, \sigma)}{\partial\,(x, x')}=\frac{\partial\,(s', \sigma')}{\partial\,(x, x')}=\frac{\partial\,(\varphi, \psi)}{\partial\,(x, x')}.$$

If the frequency distribution were known to the minutest details, the function $D\,(x, x')$ would be wholly known in its dependency on x and x'.

So the frequency scheme can by no means furnish more than the function $D(x, x')$.

Admitting $D(x, x')$ to be known, the equation

$$\frac{\partial(s, \sigma)}{\partial(x, x')} = \frac{\partial s}{\partial x} \cdot \frac{\partial \sigma}{\partial x'} - \frac{\partial s}{\partial x'} \cdot \frac{\partial \sigma}{\partial x} = D(x, x'),$$

allows us still to dispose arbitrarily of one of the functions s and σ (save its being limited to the interval between 0 and 1). If, for example, s is chosen, then σ derives from the above differential equation; hence in determining σ, a certain freedom is still left.

Having so obtained s and σ, the functions z and ζ are known too. Then we must yet assume a value of γ for determining t and t'.

A similar reasoning may be held concerning s' and σ', likewise with regard to φ and ψ. An unimodular set t, t' once being fixed, it is easy to derive a whole group of new unimodular sets t, t', submitting t, t' to the transformation group leaving invariant the form $r^2 = t^2 - 2\gamma t t' + t'^2$ and the areal increment.

These transformations, interpreted in the above non-rectangular coordinates, just are the rotations about the origin, the point $P(r, \theta)$ being carried to the point $\mathfrak{P}(r, \vartheta)$ $(\vartheta = \theta + \tau)$.

So we find

$$\frac{\mathrm{t}}{\cos\left(\frac{\omega}{2} + \vartheta\right)} = \frac{\mathrm{t}'}{\cos\left(\frac{\omega}{2} - \vartheta\right)} = \frac{r}{\sin\omega} \qquad (\cos\omega = \gamma)$$

or

$$\frac{\mathrm{t}}{\cos\left(\frac{\omega}{2} + \theta + \tau\right)} = \frac{\mathrm{t}'}{\cos\left(\frac{\omega}{2} - \theta - \tau\right)} = \frac{r}{\sin\omega},$$

whence, by eliminating r and θ,

$$T \begin{cases} \mathrm{t} = \dfrac{\sin(\tau + \omega)}{\sin\omega} t - \dfrac{\sin\tau}{\sin\omega} t' \\[2ex] \mathrm{t}' = \dfrac{\sin\tau}{\sin\omega} t - \dfrac{\sin(\tau - \omega)}{\sin\omega} t' \end{cases} \qquad \ldots\ldots\ (9)$$

Thus: the functions t, t' may occasionally be transformed by the continuous group T having one parameter. Further we may apply the reflection $S\begin{pmatrix}\mathrm{t} = t' \\ \mathrm{t}' = t\end{pmatrix}$ against the internal bisector of $\angle(tOt')$, likewise the reflection $S'\begin{pmatrix}\mathrm{t} = -t' \\ \mathrm{t}' = -t\end{pmatrix}$ against the external bisector of $\angle(tOt')$, hence also their product $SS'\begin{pmatrix}\mathrm{t} = -t \\ \mathrm{t}' = -t'\end{pmatrix}$ which effects a rotation of π about O. This rotation being also furnished by a transformation T

(with $\tau = \pi$), we may build up all the transformations considered out of the continuous group T and the finite (cyclic) group S of order 2.

In future we shall not make any use of this reflecting transformation, which only implies a change of names.

Thus it has been proved that — even if the function $D(x, x')$ were completely known — it is impossible to determine the functions t and t' without adding new arbitrary data. The question is now to choose these data in such a way that the solution should be of some practical value.

The following example shows clearly that "to establish a linear correlation" becomes an indeterminate problem as soon as functions of both variables are admitted.

If between two quantities t and t' there exists linear correlation, with the unimodular formula

$$dW = \frac{\sqrt{1-\gamma^2}}{\pi} e^{-(t^2-2\gamma t t'+t'^2)}\, dt \,.\, dt',$$

then by substituting

$$t = \frac{T-T'}{\sqrt{2}} \quad , \quad t' = \frac{T+T'}{\sqrt{2}} \quad , \quad dt \,.\, dt' \rightleftarrows dT \,.\, dT'$$

we obtain

$$dW = \frac{\sqrt{1-\gamma^2}}{\pi} e^{-1/2[(T-T')^2-2\gamma(T^2-T'^2)+(T+T')^2]}\, dT \,.\, dT' =$$

$$= \frac{\sqrt{1-\gamma^2}}{\pi} e^{-[(1-\gamma)T^2+(1+\gamma)T'^2)]}\, dT \,.\, dT'.$$

Hence between the new (not unimodular) variables T and T' there exists linear correlation with a coefficient of correlation zero; that is to say: T and T' are wholly independent. In this case no one will prefer the variables T and T' to t and t', as the really existing correlation between the original variables t and t' suggests a dependence between these variables. It is just this property of suggesting a certain dependence that makes correlation so important.

If the original variables x and x' are not linearly correlated, the frequency scheme yet pointing to some dependence, we will firstly try to establish a linear correlation between a function t only of x, and a function t' only of x'. Should this prove to be impossible, we shall try to obtain at least one variable t (resp. t') depending on only one variable x (resp. x'). If this attempt also fails, we shall try to introduce one function t (resp. t') which varies but little by the influence of x' (resp. x), and, at the same time, to obtain a correlation as large as possible, since just a high degree of correlation in interpretation will give interesting results. Moreover it will appear from the following reasoning that, though we have found two functions of x and x' linearly correlated, we shall yet continue our investigations in order to obtain functions giving more palpable results in biological interpretation; at the same time we shall be mindful of raising — as far as circumstances allow — the degree of correlation (measured by the value of the coefficient of correlation).

In discussing the canonic forms we have taken this point of view that $D(x, x')$ is fully known as function of x and x'. But in reality it is not so. The real data are several values of the integral

$$\int\limits_{\xi_k-\frac{c}{2}}^{\xi_k+\frac{c}{2}}\int\limits_{\xi'_l-\frac{c'}{2}}^{\xi'_l+\frac{c'}{2}} D\,.\,dx\,.\,dx' = y_{kl} = \frac{Y_{kl}}{N} \quad . \; . \; . \; . \; . \quad (6^a)$$

Thus we shall have to resort to these integral-values.

As we always have to operate with the class-limits, we shall introduce them into the notation. So we put

$$\xi_k + \frac{c}{2} = x_k \;,\quad \xi'_l + \frac{c'}{2} = x'_l \quad . \; . \; . \; . \; . \; . \quad (10)$$

hence

$$\xi_k - \frac{c}{2} = x_{k-1},\quad \xi'_l - \frac{c'}{2} = x'_{l-1}\,.$$

It will be easy furtheron to designate the class-centres ξ_k, ξ'_l by broken indices. So we put at the same time

$$\xi_k = x_{k-1/2} \;,\quad \xi'_l = x'_{l-1/2} \quad . \; . \; . \; . \; . \; . \; . \quad (10^a)$$

The lower limit x_0 (resp. x'_0) need not coincide with $\xi_1 - \frac{c}{2}$, $\left(\text{resp. } \xi'_1 - \frac{c'}{2}\right)$, nor the upper limit x_n (resp. $x'_{n'}$) with $\xi_n + \frac{c}{2}$, $\left(\text{resp. } \xi'_{n'} + \frac{c'}{2}\right)$.

Hence

$$\int\limits_{x_{k-1}}^{x_k}\int\limits_{x'_{l-1}}^{x'_l} D(x, x')\,.\,dx\,.\,dx' = \frac{Y_{kl}}{N} \quad . \; . \; . \; . \; . \quad (6^b)$$

In order to arrive at an exponential function of the form $e^{-(t^2-2\gamma t t'+t'^2)}$ — starting from this rectangular integral —, we shall next examine the case of linear correlation.

Chemistry. — „*Equilibria in systems in which phases, separated by a semipermeable membrane.*" XI. By F. A. H. SCHREINEMAKERS.

(Communicated at the meeting of September 26, 1925).

Systems in which a substance different to water diffuses through the membrane.

Although the preceding considerations are valid generally, also when substance different to water is diffusing through the membrane, yet we shall consider a single case more in detail. Firstly we take the osmotic equilibrium

$$E = L_1 \,\vdots\, L_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

of two liquids; we shall represent the composition of L_1 by $x_1 X + y_1 Y \ldots \ldots + (1 - x_1 - y_1 \ldots .)\ W$, that of L_2 by substituting the index 1 by 2. If water (W) is the diffusing substance, then, when δn quantities of water diffuse from L_2 towards L_1, the thermodynamical potential of L_1 increases with:

$$(\varphi_1)_W \,.\, \delta n \text{ in which } (\varphi_1)_W = \left(\zeta - x\frac{\partial \zeta}{\partial x} - y\frac{\partial \zeta}{\partial y} \cdots\right)_1,$$

that of L_2 decreases with:

$$(\varphi_2)_W \,.\, \delta n \text{ in which } (\varphi_2)_W = \left(\zeta - x\frac{\partial \zeta}{\partial x} - y\frac{\partial \zeta}{\partial y} \cdots\right)_2$$

and that of the total system increases, therefore, with:

$$[(\varphi_1)_W - (\varphi_2)_W] \,.\, \delta n \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

If the component X is the diffusing substance, then, when δn quantities of X diffuse from L_2 towards L_1, the thermodynamical potential of L_1 increases with:

$$(\varphi_1)_X \,.\, \delta n \text{ in which } (\varphi_1)_X = \left[\zeta + (1-x)\frac{\partial \zeta}{\partial x} - y\frac{\partial \zeta}{\partial y} \cdots\right]_1$$

that of L_2 decreases with:

$$(\varphi_2)_X \,.\, \delta n \text{ in which } (\varphi_2)_X = \left[\zeta + (1-x)\frac{\partial \zeta}{\partial x} - y\frac{\partial \zeta}{\partial y} \cdots\right]_2,$$

so that the thermodynamical potential of the total system increases with:

$$[(\varphi_1)_X - (\varphi_2)_X] \,.\, \delta n \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

If other components diffuse, corresponding equations are valid then, of course.

Previously we have seen that (2) defines in which direction the water diffuses in system (1); viz. the water goes towards that liquid which has the smallest φ. For that reason we have said that $(\varphi_1)_W$ and $(\varphi_2)_W$ define the osmotic water-attraction ($O.W.A.$) of the liquids L_1 and L_2 and that the $O.W.A.$ increases with decreasing φ. The same is also true for the osmose of the substance X.

If viz. $(\varphi_1)_X = (\varphi_2)_X$ then (3) is zero for all values of δn; consequently system (1) is in osmotic equilibrium with respect to the substance X; we may say, therefore, that the $O.X.A.$ (osmotic X-attraction) of both liquids is equal.

If $(\varphi_1)_X > (\varphi_2)_X$ then, as the thermodynamical potential of the total system can become only smaller, δn in (3) must be negative; consequently X diffuses from L_1 towards L_2. We may say, therefore, that the $O.X.A.$ of liquid L_2 is greater than that of L_1.

If $(\varphi_1)_X < (\varphi_2)_X$ then in (3) δn must be taken positive; consequently X diffuses from L_2 towards L_1. Now we may say, therefore, that the $O.X.A.$ of liquid L_1 is greater than that of L_2.

Consequently, as the substance X diffuses towards that liquid, which has the smallest φ, we may say, therefore, that φ defines the $O.X.A.$ of the liquid and that the $O.X.A.$ of a liquid increases with decreasing φ.

If in the osmotic equilibrium:

$$E = L \,\vdots\, L_1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

in which L and L_1 are two ternary substances, the component Y is the diffusing substance, then must be satisfied:

$$\zeta - x\frac{\partial \zeta}{\partial x} + (1-y)\frac{\partial \zeta}{\partial y} = \left[\zeta - x\frac{\partial \zeta}{\partial x} + (1-y)\frac{\partial \zeta}{\partial y}\right]_1 \quad . \quad . \quad . \quad (5)$$

If we take in (4) a definite liquid for L_1 f.i. L_p, represented in fig. 1 by point p, then the second part of (5) has a definite value. The liquids L, which are isotonic with L_p with respect to the substance Y, are represented, therefore, by a curve $p_1 p p_2$ going through the point p. Consequently this curve is an isotonic curve with respect to the diffusing substance Y; therefore, all liquids of those curves have the same $O.Y.A.$ (osmotic Y-attraction). We shall call the isotonic curves with respect to the substance W the „isotonic W-curves" and those with respect to the substance Y the „isotonic Y-curves".

If we take in (4) for L_1 the liquid L_q, represented by point q (fig. 1), then all liquids which are isotonic with L_q with respect to Y, are represented by a curve $q_1 q q_2$. All liquids of this curve have the same $O.Y.A.$ therefore.

The same is true for the isotonic Y-curves, which go through other points f.i. through r or s.

Consequently all liquids of curve $p_1 p p_2$ are isotonic with respect to the substance Y; the same is true for all liquids of curve $q_1 q q_2$, etc. Liquids of different curves are not isotonic, however, f.i. liquid p not with q or with r_1 or with s_2 etc.

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In Communication II we have deduced several properties of the isotonic *W*-curves; they are true also for the isotonic *Y*-curves. Consequently we have:

1. Each isotonic *Y*-curve has two ends; the one is situated on the side *WY*, the other on the side *XY* of the triangle.

2. Each straight line, drawn through the point *Y*, intersects the isotonic *Y*-curve in one point only.

3. Two different isotonic curves never can intersect or touch one another.

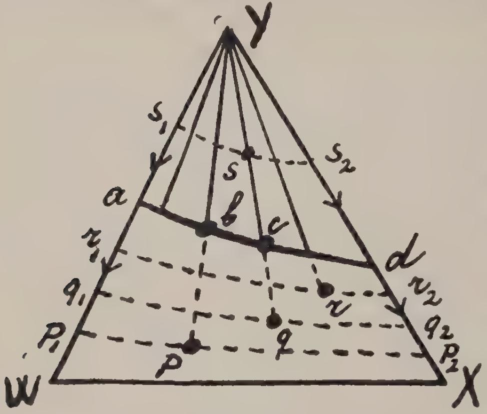

Fig. 1.

4. The isotonic *Y*-curves are straight lines in the vicinity of the point *Y*.

5. The *O.Y.A.* is equal in all liquids of an isotonic *Y*-curve; it is greater, however, the further this curve is remoted from point *Y*.

We have deduced the properties of the isotonic *W*-curves in Communication II with the aid of the ζ-surface; in exactly the same way follow the properties of the isotonic *Y*-curves, mentioned above. Of course they may be deduced also in another way. The *O.Y.A.* of a liquid L_q is viz. defined by:

$$\varphi = \left[\zeta - x \frac{\partial \zeta}{\partial x} + (1-y) \frac{\partial \zeta}{\partial y} \right]_q \quad \ldots \ldots \quad (6)$$

The *O.Y.A.* of a liquid L'_q, the composition of which differs infinitely little from that of L_q is, therefore

$$\varphi' = \varphi + \triangle \varphi = \varphi + \frac{\partial \varphi}{\partial x} \triangle x + \frac{\partial \varphi}{\partial y} \triangle y \quad \ldots \ldots \quad (7)$$

or:

$$\triangle \varphi = [-rx + (1-y)\, s]_q \triangle x + [-sx + (1-y)\, t]_q \triangle y \quad \ldots \quad (8)$$

Of all liquids L'_q which differ infinitely little from L_q we now take that liquid which arises from L_q by solution of a little *Y*. If δn quantities of *Y* dissolve in one quantity of L_q, then we have:

$$\triangle x = -\frac{x \,.\, \delta n}{1+\delta n} = -x \,.\, \partial n \qquad \triangle y = \frac{(1-y) \,.\, \delta n}{1+\delta n} = (1-y) \,.\, \delta n \quad (9)$$

so that (8) passes into:

$$\triangle \varphi = [x^2 r - 2x(1-y)\, s + (1-y)^2\, t] \,.\, \delta n \quad \ldots \ldots \quad (10)$$

The stability requires that the coefficient of δn is positive; consequently $\triangle \varphi$ is also positive for positive values of δn. With solution of *Y* in the liquid L_q the φ of this liquid increases therefore and its *O.Y.A.* decreases.

In a similar way we may deduce the general rule:

if a little of a substance dissolves in a liquid, then its osmotic attraction with respect to this substance becomes smaller.

As is already said above, this rule is true, however, only for stable liquids. Later we shall see in systems, in which dimixtion into two or more liquids can occur, that this rule is valid no more for liquids, which are unstable, in itself.

Hence follows, in accordance with the rule, mentioned above sub 5, that the $O.Y.A.$ of liquids of curve $q_1 q q_2$ is greater than that of curve $r_1 r r_2$ and smaller than that of curve $p_1 p p_2$. Consequently the $O.Y.A.$ increases in the direction of the arrows, drawn in fig. 1 on the sides YW and YX.

We now assume that the diffusing substance Y can occur as solid phase; its saturation-curve is represented in fig. 1 bij $abcd$. Consequently this is defined by

$$\zeta - x\frac{\partial \zeta}{\partial x} + (1-y)\frac{\partial \zeta}{\partial y} = \zeta_y \, . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (11)$$

in which ζ_y represents the thermodynamical potential of the solid substance Y. As the $O.Y.A.$ of an arbitrary liquid L_q is defined by (6), it follows from (11) that all liquids of curve $abcd$ have the same $O.Y.A.$ This is in accordance with the rule, deduced in Communication II.

All liquids, which are saturated with a solid substance, are isotonic with respect to this substance.

The saturation-curve $a\,b\,c\,d$ in fig. 1 is an isotonic Y-curve therefore; the isotonic Y-curves, in the vicinity of curve $a\,b\,c\,d$, must have, therefore, a corresponding form.

Consequently the isotonic curves can have several forms, just as the saturation-curves. Let us take f.i. the saturation-curve $wcdv$ of the solid substance Y in fig. 3 Comm. III. We can represent the equilibria which occur at 4°5 in the system water + alcohol + nitril of succinic acid 1) schematically by this figure, if W is water, X alcohol and Y the nitril of succinic acid. The isotonic curves of nitril of succinic acid will have in the vicinity of curve $wcdv$ a similar form with two points of inflexion.

Above we have seen that the $O.Y.A.$ of the liquids of an isotonic Y-curve is greater, the further those curves are remoted from the point Y. We now see from fig. 1 that an unsaturated solution has a greater $O.Y.A.$ and a supersaturated solution has a smaller $O.Y.A.$ than a solution saturated with Y. This is in accordance with the meaning of: saturated, unsaturated and supersaturated solution.

We now take the osmotic system:

$$L_p \mathrel{\leftarrow\!\!\!\!\!\mid\;} L_r \quad \text{fig. 1} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (12)$$

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1) F. A. H. SCHREINEMAKERS, Zeitschr. f. Phys. Chem. 27, 144 (1898).

in which, as according to fig. 1, L_p has a greater $O.Y.A.$ than L_r, the substance Y shall diffuse in the direction of the arrow. Consequently in fig. 1 L_p shifts from point p along the line pY towards Y and L_r from point r along the line Yr away from Y. The diffusion of the substance Y continues, till both liquids reach a same isotonic Y-curve f.i. curve $q_1 q q_2$.

In the osmotic system:

$$L_p \overset{|}{\underset{|}{\leftarrow}} Y + L_c \quad \text{fig. 1} \quad \ldots\ldots\ldots \quad (13)$$

the substance Y diffuses in the direction of the arrow, as follows from fig. 1. Now is formed one of the osmotic equilibria:

$$E = L_b \mid Y + L_c \ \ldots \quad (14^a) \qquad\qquad E = L'_p \mid L'_c \ \ldots\ldots \quad (14^b)$$

If viz. a sufficient quantity of solid Y is present, then L_p of (13) passes into the saturated liquid L_b of (14^a); if in (13) there is too little solid Y, then arise the two unsaturated liquids of (14^b); if both liquids are situated f.i. on the isotonic curve $r_1 r r_2$ then L'_p is represented by the point of intersection of this curve with the line pY and L'_c by the point of intersection of this curve with the line Yc.

Consequently the disappearance of the solid substance Y from (13) when passing into (14^b) is here a consequence of the diffusion of the substance Y itself and not, as we have seen several times in the previous communications, a consequence of diffusion of water.

If we assume that the solid substance Y forms a hydrate H, then we may represent the saturation-curve of H by curve $wcdv$ of fig. 1 Communication IV. The dotted curves of this figure are isotonic W-curves. We have called in this Communication IV point w the finishing-point of this curve rich in water and point v the point poor in water. Then we have found the rule:

The $O.W.A.$ of a liquid of a saturation-curve of a hydrate is greater, the further this liquid is remoted from the finishing-point of this curve rich in water.

Consequently the $O.W.A.$ of the liquids must increase in the direction of the arrows along this curve. We may call point w the finishing-point of curve $wcdv$ poor in Y and point v the point rich in Y. Then we find the rule:

the $O.Y.A.$ of the liquids of a saturation-curve of a hydrate of Y is greater according this liquid being situated further from the finishing-point of this curve rich in Y.

Consequently we have to give the opposite direction to the arrows in fig. 1. Comm. IV.

Of course the isotonic Y-curves have quite another proceeding than the isotonic W-curves, drawn in the figure; we have to imagine the points m n and o, which we shall call now m_1 n_1 and o_1, to be situated on the side YX. Then point o_1 is situated the closest to Y, point m_1 the farthest from Y. Drawing this curve we must bear in mind the rule, already previously deduced:

an isotonic curve and a saturation-curve are situated in the vicinity of their point of intersection either both within the conjugation-angle or both within the supplement-angle; if one of those curves touches the one leg of the angle, then the other curve touches the other leg.

In point c of fig. 1 Comm. IV the conjugation-angle is $H\,c\,Y$; the saturation-curve is situated out of this angle, consequently within the supplement-angle; the isotonic Y-curve going through point c must, therefore, be situated also within this angle. If we imagine to be drawn from Y to curve $w\,c\,d\,v$ a tangent, which touches this curve in point r (not drawn) then $H\,r\,Y$ is the conjugation-angle. As the saturation-curve touches the leg $r\,Y$, the isotonic curve must touch, therefore, the leg rH.

In the osmotic system:

$$L_b \overset{|}{\underset{|}{\leftarrow}} L_d \quad \text{fig. 1 Comm. IV} \; . \; . \; . \; . \; . \; . \; . \quad (15)$$

L_b has a greater $O.Y.A.$ than L_d; consequently the substance Y diffuses in the direction of the arrow in (15). Therefore liquid L_b shall separate solid H and pass into another liquid of the saturation-curve, f. i. into L_c. Then liquid L_d passes into an unsaturated liquid L'_d, which is represented by the point of intersection of the line Yd with the isotonic Y-curve $n'c\,n_1$ going through point c. Consequently system (15) passes into the osmotic equilibrium:

$$E = H + L_c \;\vdots\; L'_d \quad \text{fig. 1 Comm. IV} \; . \; . \; . \quad (16)$$

The complex of the liquids L_b and L_d of (15) is represented by a point s on the line $b\,d$, not-drawn in the figure. As the quantities of the substances in the total system do not change by the diffusion, the complex of system (16) must be represented also by this point s. The complex $H + L_c$ is represented by a point on the line Hc, which we shall call c'; liquid L'_d is situated in the point of intersection d' (not-drawn) of line Yd and the isotonic Y-curve going through c. Consequently the line $c'd'$ must go through the point s.

In the osmotic system:

$$L_b \overset{|}{\underset{|}{\leftarrow}} L_f \quad \text{fig. 1 Comm. IV} \; . \; . \; . \; . \; . \; . \; . \quad (17)$$

the substance Y diffuses from L_f towards L_b, as L_b has a greater $O.Y.A.$ than L_f. Both liquids now pass with separation of the hydrate H into a liquid of curve $w\,c\,d\,v$ situated between b and f. If the complex of the two liquids in (17) is situated f.i. on the line Hd, then (17) passes into:

$$E = H + L_d \;\vdots\; H + L_d \quad \text{fig. 1 Comm. IV} \; . \; . \; . \quad (18)$$

The directly visible result of the diffusion in system (17) is, therefore, that the hydrate H is separated on both sides of the membrane; in system (15) this hydrate is separated at one side of the membrane only.

All we have deduced above, if H is hydrate of Y, viz. a compound of Y and W, is true also when Y forms a binary compound with the component X; then the point H is situated on the side YX of this figure.

If Y forms with water and X a ternary compound D, then we can represent the saturation-curve of D by curve $w\,b\,v\,d\,w$ of fig. 2 Communication IV; the dotted curves in this figure are the isotonic W-curves. The line WD intersects the saturation-curve in the points w and v; they divide this curve into two branches; we have called w the finishing-point of those branches rich in water and v the point poor in water. Previously we have deduced:

the $O.W.A.$ of a liquid of this saturation-curve is greater, the further it is remoted from the finishing-point rich in water.

Consequently the $O.\,W.\,A.$ increases along both branches in the direction of the arrows.

We now imagine in this figure to be drawn the line YD, which intersects the saturation-curve in two points; these points of intersection divide this curve into two branches. We call the point of intersection, which is situated the closest to Y the finishing-point of those branches, rich in Y, the other the point poor in Y. We now find the rule:

the $O.Y.A.$ of a liquid of the saturation-curve is greater, the further it is remoted from the finishing-point rich in Y.

We may consider fig. 2 of this communication as special case of fig. 2 in Comm. IV; here point D is situated on the side WX and is, therefore, a hydrate of the substance X. The line YD divides the saturation-curve $a\,d\,g$ into the two branches $a\,d$ and $g\,d$; point d is the finishing-point rich in Y. Consequently the $O.Y.A.$ must increase from d towards a and from d towards g; therefore, in the direction of the arrows. The dotted curves are isotonic Y-curves; consequently b and f have the same $O.Y.A.$, they are isotonic, therefore, with respect to the substance Y; the same is true for the

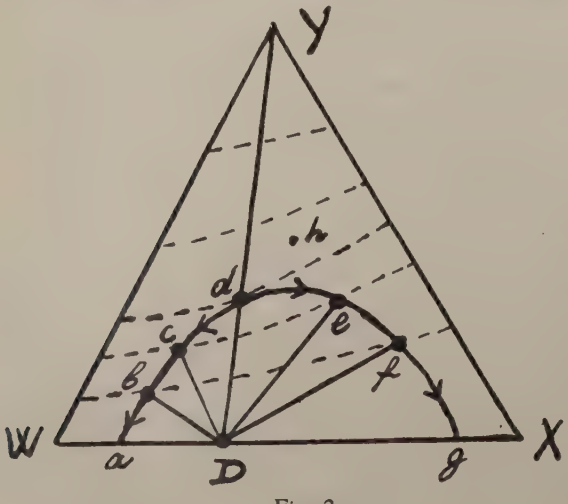

Fig. 2.

liquids c and e. The isotonic Y-curve, going through point d, touches the saturation-curve in this point d. The conjugation-angle in point c is DcY; the saturation-curve and the isotonic Y-curve are situated in the vicinity of c within this conjugation-angle; this is also the case in the points b, e and f. If the saturation-curve has such a form, that we may draw from Y a line, which touches this curve in a point r, then the isotonic Y-curve, going through r, must touch the line rD.

In the osmotic system:

$$L_h \underset{|}{\overset{|}{\rightarrow}} L_f \quad \text{fig. 2} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (19)$$

L_f has a greater $O.Y.A.$ than L_h; consequently, as is indicated in (19) by the arrow, the substance Y diffuses from L_h towards L_f. It now depends on the ratio of the two liquids in (19), which osmotic equilibrium will be formed at last; f. i. the equilibrium:

$$E = D + L_e \mid L'_f \quad \text{fig. 2} \quad . \; . \; . \; . \; . \; . \; . \; . \quad (20)$$

may arise; then L'_f is the liquid, represented by the point of intersection of the line Yf with the isotonic Y-curve, going through point e. Therefore, a result of the diffusion of the substance Y, visible at the moment, is, that a hydrate of the substance X is separated at one side of the membrane; at first sight the substance X might seem to be diffusing, instead of the substance Y.

As special case of fig. 2 we may assume that point D coincides with W or X. If D coincides with X, then of curve adg only the branch ad remains, point d of which is situated now on the side XY; the $O.Y.A.$ then also increases in the direction of the arrows, viz. from d towards a. Then, however, the isotonic Y-curve going through point d, touches no more the saturation-curve in d. If D coincides with W then of adg only remains the branch dg, point d of which is situated now on the side WY, dg now represents the solutions, which are in equilibrium with ice. Then the $O.Y.A.$ of those solutions, saturated with ice, increases also in the direction of the arrows, viz. from d towards g.

We may easily summarise the rules deduced in this and previous communications for the change of the osmotic attraction of the liquids of a saturation-curve. We take the saturation-curve of an arbitrary substance V (component or compound); we call N the diffusing substance. The line NV intersects the saturation-curve of V in one or two points; in both cases one of the points of intersection is situated between V and N; we call this the „point rich in N" of the saturation-curve. We now can say:

the $O.N.A.$ (osmotic N-attraction) of a liquid of a saturation-curve is greater, the more this liquid is situated further from the point of this curve, rich in N.

In the special case, that the solid substance, with which the liquids of the saturation-curve are in equilibrium, is the diffusing substance itself, the line NV does not exist and consequently there is no point on the saturation-curve rich in N. Then the former rule passes into:

all liquids of the saturation-curve of a substance N have the same *O.N.A.*

If we apply this rule to the saturation-curve $w\,v$ of the substance Y n the figs. 1, 2 and 3 of Communication III, then we find:

the *O.W.A.* increases along curve $w\,v$ from w towards v,
„ *O.X.A.* „ „ „ „ „ v „ w,
„ *O.Y.A.* is the same for all liquids of curve $w\,v$.

For the saturation-curve $w\,c\,d\,v$ of the hydrate H in fig. 1 of Communication IV follows:

the *O.W.A.* increases along curve $w\,v$ from w towards v,
„ *O.Y.A.* „ „ „ „ „ v „ w,
„ *O.X.A.* „ „ „ „ „ s „ w and from s towards v, if s is the point of intersection of this curve with the line HX.

For the saturation-curve $a\,d\,g$ of the hydrate D in fig. 2 of this communication we find:

the *O.W.A.* increases along this curve from a towards g.
„ *O.X.A.* „ „ „ „ „ g „ a.
„ *O.Y.A.* „ „ „ „ „ d „ a and from d towards g.

In the figs. 1—4 of Communication V the arrows indicate the direction in which the *O.W.A.* increases along the different saturation-curves; of course this is otherwise for the *O.X.A.* and *O.Y.A.* of those liquids.

We find for fig. 1 of Communication V:

the *O.Y.A.* is constant along curve $a\,c$ and increases on curve $c\,b$ from c towards b.

If we imagine viz. curve $b\,c$ to be prolongated up to a point s on the side $X\,Y$, then s is the point of this curve rich in Y; the *O.Y.A.*, therefore, must increase along this curve from s towards b, consequently also from c towards b.

For fig. 2 of Communication V we find:

the *O.Y.A.* decreases from a towards d, rests constant d to c and increases c to b.

For figs. 3 and 4 of Communication V follows:

the *O.Y.A.* is constant from a to c and increases along the curves $c\,d$ and $d\,b$ from c to b.

We now may draw easily in those diagrams schematically the isotonic Y-curves; in the vicinity of the side WX their shape comes near to straight lines; in the vicinity of the saturation-curve of Y they get corresponding forms as this saturation-curve.

(*To be continued.*)

Physiology. — "*On the Segmentation of Skeletal Muscles in the Frog.* (*Rana esculenta*)". By Dr. S. DE BOER. (Communicated by Dr. C. U. ARIËNS KAPPERS).

(Communicated at the meeting of October 31, 1925).

The question whether the fibres of skeletal muscles receive innervation from one or from different segments is a matter which has of late years engaged the attention of several investigators. On the basis of his histological researches AGDUHR [1]) came to the conclusion that in one and the same fibre of a skeletal muscle endplates of KÜHNE can be found, which are connected with nerve fibres arising from different segments. BERITOFF [2]), and also CATTELL and STILES [3]) arrived at the same conclusion after their physiological experiments, SAMOJLOFF [4]), however, basing on the results of his experiments, was induced to think that every separate muscle fibre is innervated only from one anterior root. In a previous publication I gave an extensive summary of the literature on this subject [5]), so that the above brief indications may suffice here.

The present writer studied this problem first in the M. gastrocnemius of the frog. I injected subcutaneously some drops of a veratrin solution into frogs and after the muscles had been poisoned I stimulated rhythmically one of the two innervating spinal nerves, until the veratrin curve had disappeared and twitches arose. After this an induction shock, administered to the other root, produced invariably a complete veratrin curve. If then this second root was stimulated rhythmically, until after every stimulus a twitch arose, the veratrin effect recovered itself on stimulation of the first root. That the endplates in the muscle are not the cause of the disappearance of the veratrin-effect after rhythmical stimulation of the nerve, was proved by the fact that *direct* stimulation of the muscle also produced twitches. It became evident from these experiments that the two spinal nerves innervate different parts of the M. gastrocnemious. A second series of experiments yielded the same result. I fatigued the M. gastrocnemius by applying rhythmical induction-shocks to the one root. Subsequent stimulation of the other root produced curves without signs of fatigue. (This was known before and CATTELL,

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[1]) AGDUHR. Anat. Anz. 49. p. 1. 1916; 52. p. 273. 1919.

[2]) BERITOFF. Ztschr. f. Biol. 78. p. 231. 1923; Pflüger's Arch. 205. pp. 455 and 458. 1924.

[3]) CATTELL and STILES. Amer. Journ. Physiol. 69. p. 645. 1924.

[4]) SAMOJLOFF. Pflüger's Arch. 204. p. 691. 1924.

[5]) S. DE BOER. The double innervation of the M. gastrocnemius. The Journ. of Physiol. Vol. 60 p. 215. 1925 and Verslag van de vergadering van de Amsterdamsche Neurologen Vereeniging op Donderdag 1 Oct. 1925.

and STILES supposed the explanation to be that on rhythmical stimulation the conductability of KÜHNE's endplates decreases. According to these investigators most muscle fibres contained KÜHNE's endplates, which were connected with the nerve fibres of the 8th and the 9th spinal segments). When after this the second root was again stimulated rhythmically until fatigue reappeared, the effect of the stimulation of the first root had meanwhile been considerably restored. It is seen then that during the rhythmical stimulation of the one root the fatigue recovers itself that had been previously provoked after rhythmical stimulation of the other root.

These two series of experiments have established distinctly, that in the gastrocnemius of the frog two parts of the muscle are lying side by side, each of them being innervated by one spinal nerve. However, some room was still left for the possibility that some of the muscle-fibres might be innervated from both segments. To make sure about this I registered the monophasic action-currents. To this end I first stimulated the two spinal nerves separately and after this the N. ischiadicus. It thereby appeared that after the stimulation of the N. ischiadicus the action-current curve was always equal to the sum of the two action-current curves obtained by stimulating the two spinal nerves separately ¹). This proved that none of the muscle fibres of the M. gastrocnemius receives a double innervation. Now it can be imagined that muscle fibres, innervated by the 8th and the 9th spinal nerves are intertwined in the muscle or that the gastrocnemius consists of two groups lying side by side, so that the muscle fibres of the one portion are not intertwined with those of the other portion.

This question I have set at rest. I severed the three or two spinal nerves which innervate the M. gastrocnemius, close to the spinal column; then I prepared out the N. ischiadicus together with the M. gastrocnemius and I suspended the muscle freely on the femur. If then the 8th spinal nerve was faradized, the muscle bent towards the ventral side ²); if, however, the 9th spinal nerve was faradized, the muscle contracted rather in a vertical direction or it curved dorsad. Fig. 1 illustrates this result. In some cases (once in about 15 frogs) stimulation of the 7th spinal nerve also produced a contraction of the M. gastrocnemius. These cases always showed after stimulation of the 7th spinal nerve a curving of the gastrocnemius towards the ventral side. After stimulation of the 8th spinal nerve the curvature was much less pronounced, or the direction was more vertical; after a stimulus had been applied to the 9th spinal nerve the muscle pointed dorsad, or it contracted rather in a

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¹) Communicated on the 4th Tagung der Deutschen Pharmacol. Ges. Rostock von 13—15 August 1925, The Americ. Journ. of Physiol. Vol. 75. 1925 and Ned. Tijdsch. v. Geneesk. 14 Nov. 1925.

²) By the ventral side of the muscle is meant the upper surface of the muscle, the frog lying on its back; the under-surface is then the dorsal side.

vertical direction. Once in the course of my experiments a contraction of the M. gastrocnemius occurred after stimulation of the 10th spinal nerve. In this case the muscle pointed dorsad during the stimulation of the 10th spinal nerve; after stimulating the 9th spinal nerve it was directed vertically and after stimulation of the 8th spinal nerve it curved ventral. (See fig. 5).

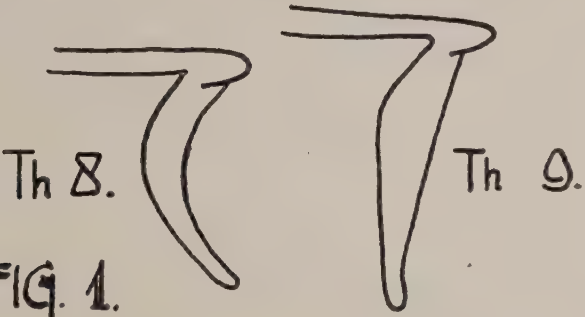

FIG. 1.

These experiments demonstrated that the fibres of the M. gastrocnemius, which are innervated by different spinal nerves, do not fall together but are arranged in groups. In order to ascertain this I slit the M. gastrocnemius lengthwise starting from the Achillestendon, and attached each part to a lever. Fig. 2 illustrates the result of this experiment. At 8 a faradic current was applied to the 8th spinal nerve, after which the ventral part contracted, while the dorsal part did not. At 9 the 9th spinal nerve was stimulated with the consequence that the dorsal part exhibits a marked contraction and the ventral part also contracts, but less than after the stimulation administered to the 8th spinal nerve. So in this muscle the dorsal part contained fibres that were innervated only by the 9th spinal nerve. They have been isolated for the major part in the dorsal portion of the muscle, while all the muscle fibres innervated by

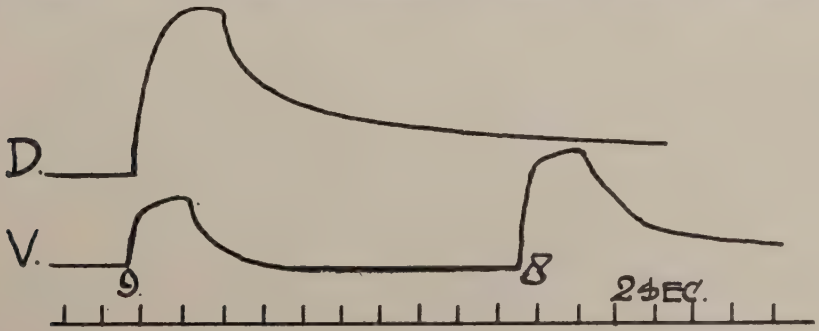

FIG 2.

the 8th spinal nerve are located in the ventral portion, in which there is also a small number of the muscle fibres innervated by the 9th spinal nerve. This experiment will be all the more successful the nearer the slit is made to the dorsal side so that the ventral portion is larger than the dorsal. If, on the contrary the slit is applied nearer to the ventral side of the muscle, so that the dorsal part is larger than the ventral, the muscle fibres innervated by the 8th spinal nerve can be partially isolated. This is instanced in Fig. 3. At 9 the 9th spinal nerve received a stimulation and contraction of the dorsal part ensued; at 8 the 8th spinal nerve was stimulated, which resulted in a contraction of both portions. It follows then that in this way we can isolate at will a part of the 8th or the 9th spinal muscular segment. I always found the 8th muscular segment on the ventral-, and the 9th on the dorsal side of the muscle [1].

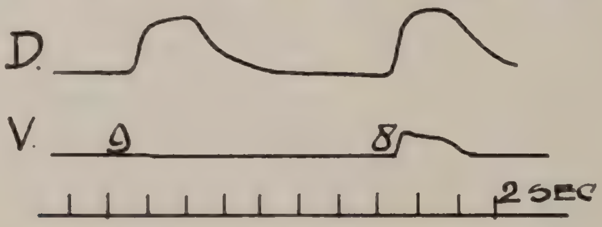

FIG 3.

These experiments, then, show conclusively that the muscle fibres of the M. gastrocnemius, innervated by the two spinal nerves are not intertwined, as they revealed to us a ventral group of muscle fibres innervated by the 8th spinal nerve, and a dorsal group that receives innervation from the 9th spinal nerve.

The experiments in which also the 7th spinal nerve innervates the M. gastrocnemius, are also of interest, as is instanced in Fig. 4. The slit was applied from the Archillestendon upwards through about the middle of the muscle. At 7 the 7th spinal nerve was faradized. A contraction of the ventral part ensued, while the dorsal part remained inactive. At 8 the 8th spinal nerve was stimulated. Now both parts of the muscle contract. At 9 the 9th spinal nerve was faradized and now arises a contraction of the dorsal part, whereas the ventral portion remains inactive. It will be seen, then, that in this preparation the muscle fibres innervated by the 7th spinal nerve are all lying in the ventral part, and those that are innervated by the 9th spinal nerve in the dorsal portion.

Both parts contain muscle fibres innervated by the 8th spinal nerve.

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[1] When speaking of spinal segments of the muscle I mean that portion of it which is located in the M. gastrocnemius. Other portions of the same myotome are lying in other muscles.

So we see that the 7th spinal muscular segment has taken the place of the 8th. The result derived from these curves stands quite in harmony

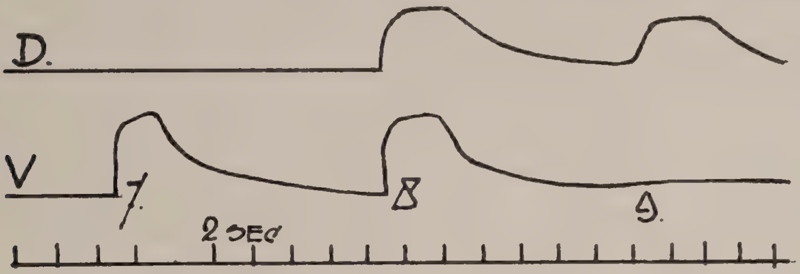

FIG 4.

with what I observed at the freely suspended muscle in those cases in which Th 7, 8 and 9 innervates part of the M. gastrocnemius. Here, indeed, we saw the same morphological changes of the M. gastrocnemius after stimulation of Th 7, viz. a curvature towards the ventral side, that I observed after stimulation of the 8th spinal nerve only in those cases, where the 7th spinal nerve does not participate in the innervation of the M. gastrocnemius. In one experiment I found that the 8th, the 9th and the 10th spinal nerves innervate the M. gastrocnemius. The curves are given in Fig. 5. They show that on stimulating the

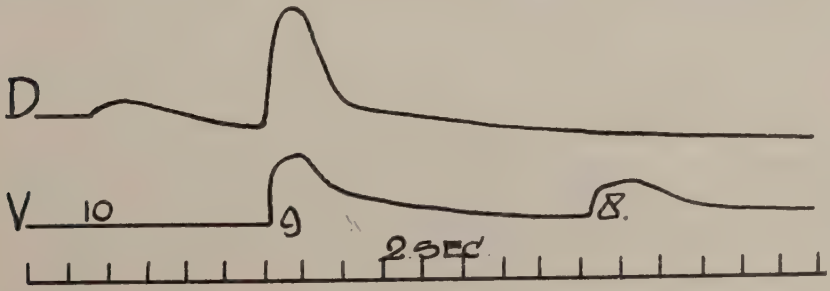

FIG. 5.

8th spinal nerve only the ventral part contracts, on stimulating the 9th spinal nerve both parts, and only the dorsal part after stimulation of the 10th spinal nerve. One question still requires further consideration. We know from segmental anatomy and above all from the work of BOLK [1]) and SHERRINGTON [1]) that the dermatomes on an extremity

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[1]) See complete literature by G. VAN RIJNBERK. Versuch einer Segmentalanatomie. Ergebn. d. Physiol. Bd. 18. S. 353. 1908.

are liable to shift in a caudal or cranial direction, according as the extremity has developed itself at the cranial or the caudal side. By a new method I have determined [1]) all the dermatomes of an extremity of one and the same animal (cat), and thereby could establish the shifting of all the dermatomes. The extremity is then, as SHERRINGTON calls it, "prefixed" or "postfixed". Now the present investigation has brought to light that also the myotomes can shift in a cranial or a caudal direction. The 7th spinal segment can be substituted for the 8th and conversely the 10th can replace the 9th. This shifting may amount to half a segment, or a quarter of it, or less. In all cases, in which the 7th or the 10th spinal nerve innervates the M. gastrocnemius I found in the frog only unilateral shifting. It is clear, therefore, that shifting is not of necessity bilateral. Accordingly the position of the 8th spinal segment in the M. gastrocnemius, is not always the same and may display variations. It follows that the curving may be different after the stimulation of the 8th spinal nerve, and consequently it is clear that the myotome-parts in a muscle always present the same sequence, and can shift without disturbing this arrangement. Up to the present this had not yet been established. Once more I wish to emphasize the fact that we have to do here with fragments of myotomes. Other parts of it are lying in the other muscles.

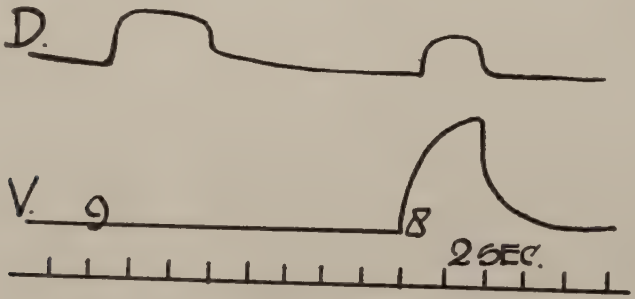

FIG. 6.

The above-mentioned experiments with longitudinal incisions in the M. gastrocnemius were also carried out with the M. Tibialis anticus longus. I cut the greater part of this muscle loose from its environment, and made a longitudinal incision down the middle between the one terminal tendon and the other. Thus the muscle was split up into a ventral-, and a dorsal part. The M. Tibialis anticus longus is innervated by the 8th and the 9th spinal nerves or by the 7th, the 8th, and the 9th. An instance of the first case is given in Fig. 6. Here we see that the stimulation of the 9th induces a contraction of the dorsal part, whereas the ventral part remains inactive. On stimulating Th 8 the dorsal part contracts slightly whereas the ventral part contracts considerably. Just as in the case of the M. gastrocnemius also here the ventral part of the muscle is innervated by Th 8, and the dorsal part by Th 9.

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[1]) S. DE BOER. These Proceedings 18, p. 1133 and 19, p. 321.

However, here also Th 7 can partake of the innervation, as appears from Fig. 7. On stimulating Th 7 there arose a contraction of the ventral part and on stimulating Th 8 a marked contraction of the ventral and the dorsal part ensued, whereas stimulation of Th 9 yielded a small contraction of the dorsal part. It will be seen, then, that also in the M. tibialis anticus longus the myotome fragments can shift without disturbing the serial arrangement, so that Th 7 takes the place of Th 8. Hence these relations appear to be similar to those established by us for the M. gastrocnemius.

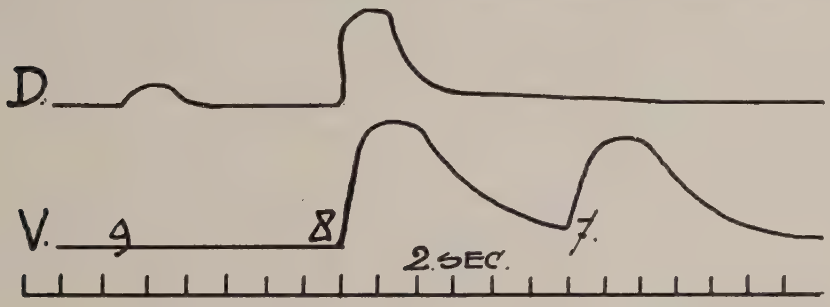

FIG. 7.

Also in this muscle there are no muscle fibres which receive a double innervation. I demonstrated this by means of the string galvanometer and found that the monophasic action-current curve, obtained after stimulation of Th 8 added to the one produced by stimulating Th 9, was equal to the action-current curve obtained by stimulating the N. ischiadicus. Just as in the present experiments with the gastrocnemius, I used also here only muscle preparations that were innervated exclusively by Th 8 and Th 9.

Next I continued my experiments with the M. rectus femoris and the M. gracilis major. In the muscle I made longitudinal incisions after I had cut loose the lower portion from its environment, and thus I split up the muscles into a medial and a lateral part. Next I stimulated the 8th and the 9th spinal nerves and registered the contractions of the medial and the lateral part on a smoked drum. It hereby appeared that the medial part of these muscles is innervated by the 8th spinal nerve and the lateral part by the 9th. In both muscles it will be necessary to ascertain by means of the string galvanometer whether in these muscles part of the muscle receives innervation from both spinal nerves.

By the methods worked out by me heretofore I purpose to prosecute my experiments also with other muscles, while at the same time I shall endeavour to collect data also from other animals.

The above results do not entitle me to draw conclusions for other muscles, as it may very well be possible that fibres of muscles with an intenser function possess a plurisegmental innervation. In a previous investigation I could establish, that the skin areas with a more intensive function are innervated from more segments than cutaneous areas with a less intense function [1]). Thus I could establish that the "overlap" of the dermatomes is more marked on the ventral side than on the dorsal side of the body. This tallies with the stronger function of the skin on the ventral side and with the smaller sensory circles of WEBER in situ on the ventral than on the dorsal side. In previous publications [1]) these relations were dwelt upon at length. Therefore we have also to consider the possibility that muscles with a more intensive function may possess fibres with a plurisegmental innervation. In this direction I shall proceed with my investigations.

When we stimulate one of the two innervating anterior roots of the freely suspended gastrocnemius, it will depend on the position of the segmental parts of the muscle concerned how much the muscle inclines towards the ventral side or whether it will point in a dorsal or in a vertical direction. If the 8th muscular segment is located along the ventral border, then a typical and pronounced curving will appear ventrad after stimulation of the 8th spinal nerve. If, on the contrary, this muscular segment extends dorsad, the curving will be less pronounced after stimulation of the 8th spinal nerve. The frequent morphological change in the various gastrocnemii implies that the position of the muscular segment is not stationary but vacillating.

The fact that the ventral or medial side of the muscles (gastrocnemius, tibialis anticus longus, rectus femoris, M. gracilis maior) receive innervation from more cranial parts of the central nervous system than the dorsal side, is perfectly in keeping with the experience of Prof. BOLK [2]). This investigator found for the upper leg and the lower leg that "the medial muscles in these groups originate from the more proximal (higher) segments, and the lateral muscles from the more dorsal (lower) ones".

My own investigation showed that this pronouncement applies not only to the entire muscle but also to parts of it.

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[1]) See S. DE BOER, These Proceedings **18**, 1915, p. 1133 and **19**, 1916, p. 321. Ned. Tijdschr. v. Geneesk. Jaargang 1916, II and Psychiatrische en Neurol. Bladen 1918. (Feestbundel WINKLER).

[2]) L. BOLK, De Segmentale Innervatie van romp en ledematen bij den mensch, Haarlem, F. Bohn 1910.

Zoology. — *"On the Thyroid Glands and on the Phylogeny of the Perennibranchiate and Derotremous Salamanders".* By Prof. J. VERSLUYS.

(Communicated at the meeting of June 27, 1925).

In the latest decennia it has become more and more evident that hormones are highly instrumental to the growth of the animal body, and to the development of several of its chief qualities. But then it is most likely that some of the modifications the animals underwent during their phylogenesis, were associated with changes in the production of the hormones. The factors that brought about the evolution of animals need not have affected the structure of the organs in a direct way only ; this may have occurred also indirectly through their influence upon the organs that form the hormones and upon the production of hormones. So the rate of development, which may be of great importance for the acclimatization and consequently for the propagation of a species, is at least sometimes under the control of the hormone-forming organs. Hereby a new point of view was brought forward for the study of evolution. It is of special importance that the production of hormones depends on the climate and probably also on the food ; changes of climate or food can through the agency of hormones modify the structure and the psychical properties of an animal. When in course of time the modifications increase, they can be either deleterious, immaterial, or useful to the animal ; consequently they can be conducive to the propagation or the extinction of the species. Perhaps in this way, an explanation can be given of the occurence of some useless properties or of such properties as are even noxious on account of their exorbitancy (DENDY 1911).

Not a few investigators have already pointed out the probable significance of hormones for evolution, e.g. CUNNINGHAM (1908, 1921), BOURNE (1911), DENDY (1911, 1923), TANDLER (1913), MAC BRIDE (1914, 1917), NOPCSA (1917, 1923), KEITH (1919), HART (1920), BOLK (1921A, 1921B, 1922) and GRAHAM KERR (1924). For Man this problem derives additional interest from BOŁK's conception that the modified hormone-production played an important part in the descent of Man from Primates, and from KEITH's theory that the differentation of Man into racial types is associated above all with a different production of hormones. It will, therefore, be undoubtedly of great importance to test these conceptions of the part played by hormones in phylogeny.

The first question we have to answer is whether any modifications in the hormone-forming organs can be found that are correlated with evolution. As far as I am aware, there is only one example of it on record, viz. that given by NOPCSA (1917). This scientist pointed to the fact that among the fossil *Dinosaurs* there exists a parallelism between an excessively enlarged groove for the hypophysis in the base of the skull (which implies an abnormally large hypophysis) and the gigantism of many of these animals, some of which are the largest of all land-animals. He compares this gigantism with the well-known pathological overgrowth in Man, designated by the name of acromegalia. This disease is very probably a direct consequence of an affection of the hypophysis, which is thereby enlarged and imparts an unusual amount of hormone to the body. It is notorious that the hormone of the hypophysis stimulates the growth. Hence NOPCSA correlates the gigantism of the *Dinosaurs* with an anomalous hypertrophy of their hypophysis.

However the assumption of such a correlation between evolution and hormone-producing organs requires additional evidence, the more so as NOPCSA's example concerns fossil-forms, of which we cannot examine the hormone-producing organ itself; we know only the groove in which it laid, and which it need not have filled up entirely. Now I believe to have found an additional case in the thyroid of the *Urodela*. Its hormone is largely instrumental in the metamorphosis of these animals, as was first demonstrated by GUDERNATSCH (1912A, 1912B, only for *Frogs*) and corroborated by a number of researchers (e.g. by HERINGA, 1922, 1924 and notably for *Salamanders* by JENSEN, 1916, HART, 1917, WINTREBERT, 1908, UHLENHUTH, 1921, 1922, HUXLEY and HOGBEN, 1922, and SWINGLE, 1923, 1924).

The administration of thyroid hormone calls forth the metamorphosis even in very young larvae, whereas withholding it through extirpation of the thyroid body prevents the metamorphosis. Now, in a number of *Urodeles*, in the *perennibranchiate* and the *derotremous Salamanders*, the metamorphosis is either completely suppressed or does not attain completion, so that the development of the animals comes to a standstill in metamorphosis: they are *neotenous*. It appears that in all these forms the thyroid deviates more or less from the normal[1]). Some reports in the literature point in this direction. So SCHMIDT, GODDARD and VAN DER HOEVEN (1862, fig. 3, see page 32) give a picture of a surprisingly large thyroid of the *Giant Salamander* Megalobatrachus maximus; the authors add the following remark: "These glands are an assemblage of blind folliculi, measuring 1—2 mm., which are filled with a colloid mass. On the whole these glands reminded us of diseased glandulae thyreoideae in Man with incipient colloid degeneration" [2]) BOLAU (1899) found in a specimen of the *Giant Salamander*, of the length of 132 cm., very large thyroids 6 cm. in length and 1½ cm. in breadth. It is also of interest that

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[1]) For the structure of the normal thyroid gland in non-neotenous *Salamanders* see BOLAU 1899, LIVINI 1902, THOMPSON 1911; and for Rana ADLER 1916.

[2]) Translated from the dutch.

VON EBNER (1877) has described a neotenous specimen of Triton cristatus 13 cm. long, of which the thyroids were excessively enlarged, measuring on either side : length 5, breadth 5, thickness 2½ mm., while the normal dimensions of the thyroid in this animal, in individuals of the same bodylength, are about long 1½ to 2, broad ¾ to 1, thick ½ mm. We see then that the thyroids of VON EBNER's larva are about 70 times the normal size. In every respect this animal possessed the structure of a larva with external gills, but it was sexually mature, and of the size of a full-grown animal. This gives reason to assume that there is in this case a correlation of neotony with the hypertrophied thyroids (VON EBNER, of course, did not think of this). Neotenous specimens of normal *Salamander*-species, especially Tritons are not rare, but EBNER's case is the only one in which some information is given on the thyroid. Presumably it is not so anomalous in other neotenous Tritons, otherwise this would have been noticed before (see MAREES VAN SWINDEREN 1925).

Opposed to these reports that point to enlarged thyroids in neotenous Salamander-forms are some others mentioning very small dimensions of these glands. So for instance the thyroid of the *perennibranchiate Salamander* Proteus is described by LEYDIG in 1863 as an extremely small, unpaired, median organ, made up of 15 to only 3 follicles of 0.12—0.15 mm. diameter (however, he has not found the paired thyroid, also present). And concerning the perennibranchiate form Typhlomolge Rathbuni miss EMERSON reports that she could not find a thyroid in a series of sections. A detailed investigation has proved that here, indeed, the thyroids are very rudimentary and are even lacking in some individuals. A normally functioning thyroid is not present here (UHLENHUTH, 1923 ; SWINGLE, 1922).

The present writer examined a number of specimens of *perennibranchiate* and *derotremous Salamanders* for the size and the structure of their thyroid glands, and compared with them the thyroids of a number of normal *Salamanders* and of a few *Axolotls,* i.e. neotenous individuals of Amblystoma mexicanum. We had some difficulty in procuring the necessary material, and the conservation also fell short. Only one individual of Siren was at my disposal. Typhlomolge I was not in a position to examine, but this is entirely made up for by UHLENHUTH's paper (1923). However, the results of my inquiry seemed sufficiently complete to justify their publication. Already in 1923 a short preliminary communication on my researches was published.

In the first place I examined the size of the thyroids in relation to the body-volume. In a number of specimens of various forms I measured the lenght, the breadth and the thickness of the thyroid which was most often paired, occasionally with accessory thyroids ; by multiplying these numbers and adding up the separate values of the two glands I obtained a number expressing the amount of thyroid-tissue present. This number I divided by the volume of the animal ; the quotient constituted the index by which forms could be intercompared, that furnished a standard to judge of the relative size of the thyroid glands.

It goes without saying that this index varies rather much individually for normal *Salamanders*, with nutritive conditions, with outward circumstances; the amount of colloid [1]) present in the thyroid is also of great importance. In my limited material I could not establish a great influence of the age of the animals. In order to get some idea of the normal relation of the size of the thyroids to that of the body in typical *Salamanders*, that is a normal index, I added up the indices of 3 specimens of Triton cristatus, 2 of Triton taeniatus and 4 of Salamandra maculosa, and divided the sum bij the number of specimens, 9. The normal index thus obtained is 0.00016921 [2]).

In this connection it should be remembered that the nature of the colloid present in the follicles influences the contraction of the thyroid when conserved in alcohol. Generally the thyroid contains a colloid so consistent as to contract little in alcohol, and to fill up the follicles almost entirely; but sometimes the thyroids in the preparations contain very little colloid, presumably because the colloid was less consistent and has contracted considerably in alcohol. Such is the case with the specimens D and C of Megalobatrachus, with Amphiuma B and with Siren, and here the thyroid has probably contracted more in alcohol than could possibly be the case with a normal consistence of the colloid. In life the thyroids of these specimens were probably larger than is expressed by the indices.

The text-figures A and B represent the thyroids of some of the forms examined; figure B, in which all the heads have been reduced to the same length, gives a good idea of the marked differences in the size of the thyroids.

For a number of neotenous forms and for some specimens of Amblystoma I found the indices given in the table page 833.

When surveying this table we see that in some of the neotenous forms the thyroids are enlarged, in others more or less reduced, and that these differences do not occur in a disorderly way: a hypertrophy of the thyroid is found in all specimens of *Derometremata* examined and in Siren; a reduction is observed in all the other *Perennibranchiates*. This is very evident in Proteus and according to UHLENHUTH also in Typhlomolge. In these two forms the thyroids are not only very

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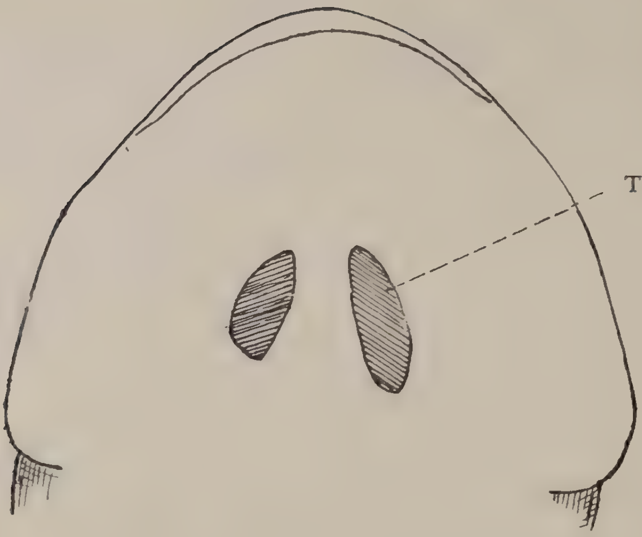
[1]) On the difference in the size of the thyroids in Rana temporaria from various regions, see ADLER, 1916.

[2]) The indices were for Triton cristatus: spec. A, long 125 mm., 0.0003947; spec. C, long 128 mm., 0.000109; spec. B, long 148 mm., 0.0001688; for Triton taeniatus: spec. B, long 86 mm., 0.0001732; spec. D, long 85 mm., 0.0002142; for Salamandra maculosa: spec. B, long 166 mm., 0.00017; spec. A, long 168 mm., 0.0001213; spec. C, long 161 mm., 0.0000931; spec. D, long 141 mm., 0.0000786. Specimen A of Triton cristatus exceeds the normal.

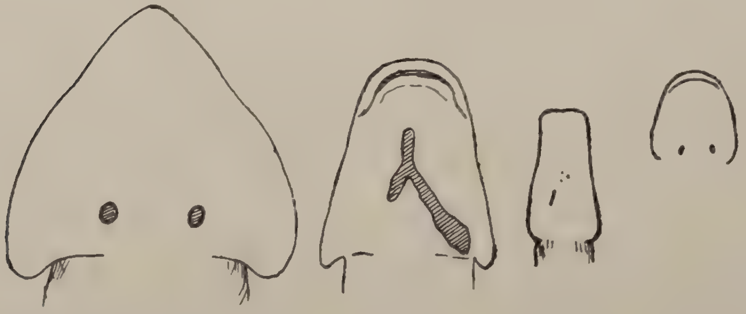
Indices of the Thyroid Glands in some neotenous Urodela and in an Amblystoma tigrium, adult.

Species	Length mm	Body volume cm^3	Index	Size of the Thyroids
Necturus spec. C	168	21	0.000107	about $^{2}/_{3}$ normal
" spec. A	255	83	0.000189	normal
" spec. B	408	552	0.000065	$^{2}/_{5}$ normal
Proteus spec. A	150	5	0.000025	$^{1}/_{6}$ normal
" spec. B	215	15	0.000028	$^{1}/_{6}$ normal
" spec. C	240	20	0.000012	$^{1}/_{14}$ normal
Siren spec. A	514	297	0.000469	± 3 × normal
Megalobatrachus maximus spec. A	175	28	0.000342	2 × normal
" spec. B	380	260	0.000785	nearly 5 × normaal
" spec. D	600	2880	0.000433	rather more than $2^{1}/_{2}$ × normal
" spec. C	790	4400	0.000231	nearly $1^{1}/_{2}$ × normal
Cryptobranchus alleghaniensis spec. B	250	65	0.000343	rather more than 2 × normal
Amphiuma spec. B	550	162	0.000355	" " " 2 × normal
" spec. A	710	380	0.000326	" " " 2 × normal
Amblystoma larve *(Axolotl)* spec. D	186	50	0.00121	" " " 7 × normal
" spec. C	234	63	0.00054	3 × normal
Amblystoma tigrinum spec. A	230	40	0.000343	2 × normal

small, but they also display an aberration in their development. Whereas the normal *Urodela* have a paired thyroid (see fig. A, 5), a third, more forward, median, unpaired thyroid is present in Typhlomolge as described bij UHLENHUTH. Most often one of the three thyroids is lacking, sometimes no thyroid could be detected at all. In Proteus I found a similar condition, only the reduction is less marked, and I could always find thyroids, though in two specimens one of the paired thyroids was absent (fig. A 4), once on the left, and once on the right. I find the follicle-epithelium in Proteus distinctly flattened, which is suggestive of a feeble function. In Necturus the reduction of the thyroid is much less pronounced, but the follicles are very large, their mean diameter being twice that in the normal adult *Salamanders* (I compared Salamandra maculosa and Onychodactylus japonicus), so their volume is 8 times larger. It follows, then, that the surface of the follicle epithelium in Necturus must be proportionately smaller than in normal *Salaman-*

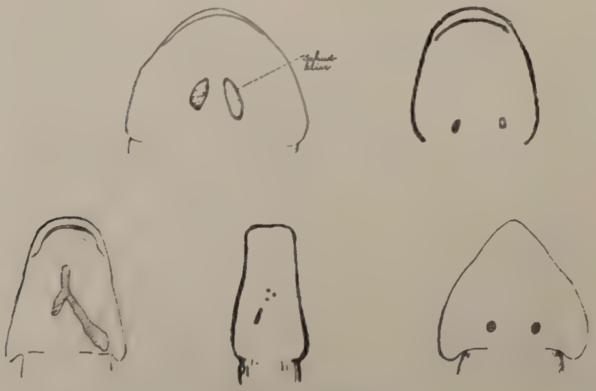


1. Megalobatrachus maximus (spec. D).



2. Necturus maculatus (spec. B).
3. Siren (spec. A).
4. Proteus (spec. B).
5. Salamandra maculosa (spec. D)

Text-figure A,
Thyroids of some *Urodeles* in situ. All figures $^2/_3$ nat. size.



Text-figure B.
The same figures as in fig. A, but all reduced to the same length.

ders; the considerable amount of colloid in the follicles has caused the thyroid to expand, but its productive surface is smaller than normal (about half). So we find in three forms of the *perennibranchiate Salamanders* a thyroid that is reduced and there is *hypofunction.* The reduction of the thyroid is most pronounced in Proteus and Typhlomolge, which also display the greatest anomaly, the more pronounced secondary adaptations, in their bodystructure. In Necturus the reduction of the thyroids is much less, while their histological structure is still normal, with a slightly flattened cubic epithelium of the follicle wall; this form in its body structure deviates little or not at all from a normal larva of *Urodeles.*

Quite different is the transformation of the thyroids in the *Derotremes* and the *Perennibranchiate Siren* (in so far as we may form an estimate of the relations in the latter form from one individual). The thyroids are not reduced, but enlarged, as a rule two or three times. This is also the case, when only a small part of the follicles in the alcohol-material is filled with colloid, so that the thyroids are contracted more than is the case with a normal consistence of the colloid (see page 832). Indeed, in some of the specimens examined the dimensions of the follicles are larger than in normal *Salamanders,* but at the same time the consequent diminution of the secreting surface is mostly more or less compensated by a folding of the follicle-wall (in a very marked degree in Amphiuma, spec. B; see fig. 3, plate) or by the irregular shape of the follicles (as in Amphiuma A, fig. 4, plate). In other specimens, i.a. in Megalobatrachus, spec. A, 175 mm. long, (which has almost entirely lost the external gills, except a few remains, but which still has an open gill-slit) the follicles are smaller than normally, so that the secernent surface is still more enlarged than would follow from the hypertrophy of the whole thyroid. In Siren the follicles appear to be as large as in normal *Salamanders.* It is, however, of special importance that in the *Detotremes* and Siren I invariably found the follicle-epithelium highly cylindrical (fig. 8, 9, plate), for this points to *hyperfunction.* The occasional formation of papillae by the epithelium (fig. 9) also points in this direction. The figures given us by the *Derotremes* bear some resemblance to those of the human thyroid in BASEDOW's disease, in struma parenchymatosa, which is also attended with a hyperfunction of the thyroid (see KOCHER 1912, BREITNER 1924); there we often meet with cylindrical epithelium, with papillae-growth and hypertrophied follicles of very irregular shape with folded wall, like the preparation of Amphiuma spec. B., represented by fig. 3.

The thyroid of the *Derotremata* and of Siren apparently functions vigorously. In this process we must assume the product to be supplied to the body [1]); anyhow the follicles only exceptionally contain colloid of more viscous consistence, which displays the typical breaking up in columns in the preparations of alcohol material (e.g. in a specimen of Megalobatrachus, of which Mr. DE FREMERY furnished the material (see plate fig. 5). Most often the follicles in the preparations are for the greater part empty, just as with struma parenchymatosa. This strikes us all the more, when we compare the thyroid of the *Axolotl*. This is pretty much enlarged (see table p. 833), chiefly in consequence of an accumulation of colloid, through which the follicles are considerably distended and their epithelium is completely flattened (fig. 6, 10, plate). Here the colloid is detained in the thyroid and in consequence the function of the epithelium decreases as is evident from the intense flattening. It can be concluded from the non-appearance of the metamorphosis that there is a hypofunction though the thyroids are enlarged, a condition which, if it should become pathological, would be comparable to colloid goitre (VON EBNER's larva with its 70 times enlarged thyroids, shows that goitre is possible also in *Urodeles*.)

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[1]) The colloid is probably not identical with the thyroid hormone which, however, is decidedly present in the colloid.

It follows from the above observations that the thyroid of the *perennibranchiate* and the *derotremous Salamanders* is developed abnormally and that two types are to be distinguished:

a. The reduced to rudimentary type with hypofunction of the *perennibranchiate Salamanders* Necturus, Proteus and Typhlomolge.

b. The enlarged type with hyperfunction of the *derotremous Salamanders* and of the *perennibranchiate* Siren.

With regard to the second type, however, the question may be asked whether the secretion of the thyroid contains sufficient normal hormone, whether there is perhaps a dysfunction. It would seem to me that dysfunction is no less probable than an overproduction of normal hormone. I am led to think so in virtue of the interesting researches by ADLER (1916). In his cultures of larvae of Rana temporaria first at a high temperature (30°—32° C.), and then at low temperature (8°—10°) he obtained numerous larvae that did not metamorphose or were late and tardy in doing so. The thyroid of these larvae appeared to be hypertrophied, grew strongly and exhibited in preparations the typical aspect of a *Basedow-thyroid ;* the form of the follicles is irregular, many new follicles are formed, the follicle-epithelium is cylindrical; the colloid in the follicles shows less and less affinity to stains, and grows less and less viscous. So it is clear that the thyroid functions vigorously; the non-appearance or the retardation of the metamorphosis cannot be due to a feeble functioning of the thyroid, it must be ascribed to the quality of the product, which is insufficient. As the thyroid of the *derotremous Salamanders* and of Siren reveals a similar transformation and the very tardy metamorphosis implies a lack of hormone, there is some reason to assume a dysfunction also here.

Now, in this connection it is of paramount significance that, just as there are two types of transformation of the thyroid, there are also two types of neoteny among the permanently neotenous forms of the Urodeles (VERSLUYS 1909, 1912, 1923) and that these two coincide.

Necturus, Proteus and Typhlomolge are completely in the developmental stage of an Urodele-larva, just before the metamorphosis. They correspond in their structure with *Axolotls* and the not unfrequent neotenous, perennibranchiate specimens of Triton and other *Salamanders*. Like these they must have originated suddenly, because the metamorphosis stayed away, yet the animals became sexually mature and could propagate. That this neoteny is hereditary, we know from the Axolotl and has been demonstrated by DE FREMERY and VAN SWINDEREN for a neotenous race of Triton taeniatus (DE FREMERY 1924; VAN SWINDEREN 1925). The neoteny of Megalobatrachus, Cryptobranchus, Amphiuma, Siren, and the related Pseudobranchus however is a quite different one; these animals do not make a halt before the metamorphosis; they commence it, indeed, but they do not finish it. It cannot be that the metamorphosis is here quite suppressed; it is only retarded and not completed. This transformation may have been reached very gradually; the metamorphosis was then at first still almost completed [1]), subsequently more and more incomplete [2]), until even the external gills were retained in Siren. On the other hand in several respects the structure of Siren is not purely larval, but resembles that of a full-grown animal or anyhow of a *Salamander* in its metamorphosis, which is evident from the well-developed lungs, from the auditory ossicle, from the interruption of the larval palatinum-quadrate bone-junction, from the structure of the olfactory organ with JACOBSON's organ, and from the occurrence of an independent coracoidbone in the shoulder-girdle. In consideration of this combination of larval structure with that of adult *Urodeles* Siren cannot be conceived to have originated suddenly through suppression of the metamorphosis, but only through a gradual slowing and retrogression of the metamorphosis which was lengthened out, just as in the derotremous forms. Although Siren and Pseudobranchus possess external gills like the *perennibranchiate Salamanders* Necturus, Proteus and Typhlomolge, the type of their neoteny is not that of these forms, but is completely the same as that of the *Derotremata*. Now it is remarkable that also the transformation of the thyroid in Siren resembles that of the *derotremous Salamanders* and is unlike that of the other *Perennibranchiates*.

The specimen of Siren examined by me has peculiarly shaped thyroids which extend forward to a considerable distance and unite there to an unpaired median part, corresponding to the processus pyramidalis of the human thyroid (fig. A 3).

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[1]) As still is the case in the *Giant-Salamander*, that does not only shed the external gills, but also shuts its gill-clefts, though it be only after years.

[2]) *Cryptobranchus* and *Amphiuma* in which the gill-clefts are always open, and the skeletal gill-arches remain larval.

In the typical *perennibranchiate Salamanders* Necturus, Proteus and Typhlomolge, the larval structure is retained completely; so their neoteny is a *complete* one, and the thyroid is reduced to rudimentary, with hypofunction. *Derotremata* and Siren retain the larval form only in part; their neoteny is *incomplete,* and the thyroid of these forms is enlarged with hyperfunction, which probably goes hand in hand with a dysfunction. Here we should bear in mind that the various neotenous forms must have originated independently: they are not interrelated except Siren and Pseudobranchus, and perhaps also Megalobatrachus and Cryptobranchus. *Three times the complete neoteny arose independently in* Necturus, Proteus *and* Typhlomolge, *and in this process the transformation of the thyroid invariably went in the same direction: hypofunction and reduction. The incomplete neoteny also arose at least three times; once in* Amphiuma, *a second time in* Megalobatrachus *and* Cryptobranchus, *and a third time in* Siren *and* Pseudobranchus; *in this case there is always enlargement of the thyroid with hyperfunction.* This points to a correlation of the way in which the thyroid is modified and the type of the neoteny.

What conclusion can we now deduce from these observations with respect to the causes of the neoteny of perennibranchiate and derotromous Salamanders?

There is reason to look for the cause of the neoteny in a shortage of hormone, which brings about retardation or total absence of the metamorphosis. In the completely neotenous *Axolotl* the metamorphosis can be elicited by the administration of a larger amount of hormone 1), so that in this form the neoteny can be unreservedly ascribed to a shortage of hormone (see SWINGLE 1924). This also affords a plausible explanation for the neoteny of Necturus, Proteus and Typhlomolge with their reduced thyroids. However, another explanation also suggests itself, viz. that for some reason or other the body no longer reacts with metamorphosis on the thyroid-hormone (UHLENHUTH 1921). SWINGLE (1924) believes that this must be somewhat the case in the *Axolotl.* Neither do Necturus and Proteus 2) react any more on the administration of thyroid hormone (JENSEN, 1916; SWINGLE, 1924). The degeneration of the thyroids then would result from the suppression of the metamorphosis. But just this is very improbable, for if the normal development of the thyroid were really so closely bound up with the metamorphosis, we might also expect in normal *Salamanders* after the metamorphosis an atrophy of the thyroids. The two cases are comparable.

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1) Here the thyroid produces rather much hormone but retains too much of it, instead of supplying the hormone to the body.

2) Since the fourth arterial arch has disappeared here these forms could not metamorphose completely, nevertheless this process might commence for all that (see BOAS, 1881).

Now, since an atrophy of the thyroid after the metamorphosis does not appear in these animals, and since on the other hand the thyroids continue to grow considerably, keeping pace with the growth of the body, we can neither assume that the degeneration of the thyroids in the neotenous Salamander forms results from the neoteny. The relation must be the reverse, viz. the neoteny resulted from the dysfunction of the thyroids, because the body did not receive sufficient hormone. That the two forms of neoteny, the complete and the incomplete form, present either of them a type of transformation of the thyroid of their own also speaks for a far closer correlation than would exist with a passive degeneration of the thyroids as a result of the suppression of the metamorphosis.

For an explanation of the occurrence of the neoteny let our starting point be a shortage of hormone. Then there are still two possibilities to be considered : 1⁰ this shortage may result from an insufficient production of normal hormone, 2⁰ it may also be that the thyroids do not impart an adequate amount of hormone to the body, but retain it and deposit it in the colloid. The latter is probably the case with the *Axolotl* (UHLENHUTH, 1919, 1923 ; SWINGLE 1922, 1923 A, 1924). There the thyroid resembles that of Man in colloid-goitre (p. 836), which is a consequence of an inhibited emission of secretion to the body (BREITNER 1924). A factor is missing, which makes the thyroids deliver their hormone ; this factor may be a nerve stimulus, or an hormone from the anterior lobe of the hypophysis, or it may arise from a deficient circulation, or lack of oxygen (on the latter factor see BREITNER 1924, p. 4, after MANSFELD-MÜLLER). In this way the complete neoteny of Necturus, Proteus and Typhlomolge can readily be interpreted. By some cause or other the thyroids no longer emitted their hormone, hence they lost their signifiance and ultimately they became smaller and degenerated. Owing to the retention of the hormone all at once a complete neoteny was engendered, as is typical of these animals.

This interpretation does not apply to the *derotremous forms* and Siren, as in them hormone is indeed imparted to the body, which is obvious from the fact that metamorphosis commences. Besides this we have already observed that the structure of the thyroid here points to a hyperfunction and quick emission of the secretion to the body. Most likely we have to do here with a dysfunction, so that the thyroids, although functioning vigorously, and emitting their secretion, yet cannot supply the normal quantity of hormone required by the body (p. 836). The phylogeny of these forms may be imagined to be as follows : The increasing dysfunction of the thyroids retarded the metamorphosis, which began ever later and lasted longer ; the animals became sexually mature in their metamorphosis and did not accomplish their metamorphosis. This was gradually lengthened out, it was still gone through entirely, or partly for some points of their anatomy, for others only for a small part or not at all. Here accommodation to outward circumstances can have been of great influence. The thyroids tried to make up for the shortage of hormone bij enlarging, but they did not succeed in filling up the deficiency.

Thus the two types of neoteny as well as the associated types of transformation of the thyroids can be explained and correlated. We think that we have to look for the cause of the neoteny, for the origin of the *perennibranchiate and derotremous Salamanders* in the thyroid. Either a change in the hormone production or in the supply of hormone to the body was the cause of the origin of these forms, which could develop to quite new types among the *Urodeles*. This transformation was achieved in the open air, and inadequate forms could not survive; only those forms persisted that were suited to their environment or could soon adapt themselves to it. For the ancestors of the *Derotremata* and of Siren an evolution from a more terrestrial life to a permanent aquatic existence can in this connection have been of influence, because the metamorphosis lost part of its importance for the animal by this change.

Lastly the question may be raised what might then have been the cause or the causes of the irregular function of the thyroids. All sorts of factors can have come into play here. It may have been want of iodin or an influence of the changes in the vascular system during the metamorphosis. It cannot be said whether this supposition is right or not.

Summary.

1. The neoteny of the *perennibranchiate* and *derotremous Salamanders* goes hand in hand with an abnormal development of their thyroids. As the hormone of the thyroid controls the metamorphosis, a case is given here in which the phylogenesis of entirely new animal forms is associated with a change in an endocrine organ closely related with it.

2. Among *Urodeles* there are two types of neoteny: that of the *perennibranchiate forms* proper Necturus, Proteus and Typhlomolge, which in their structural development persist in the stage of the full-grown *Urodele*larvae, before the metamorphosis, and that of the *derotremous forms* Megalobatrachus, Cryptobranchus, Amphiuma and of Siren and Pseudobranchus, which begin their metamorphosis, but do not accomplish it. An entirely different transformation of the thyroids coincides with this. In the first type the thyroids are small to rudimentary, and there is apparently a hypofunction of the thyroids. In the second type the thyroids are enlarged, and there is apparently a hyperfunction of the thyroids, probably associated with a dysfunction. Since the two types of neoteny have originated several times independently of each other, and yet the transformation of the thyroids in each type always went in the same direction, a close relation must needs be assumed between the neoteny and the mode of transformation of the thyroids.

3. The cause of the complete neoteny of the *perennibranchiate forms* is probably to be found in the retention of the hormone in the thyroid, which induced a complete suppression of the metamorphosis. The thyroids lost much of their significance, when they could no longer supply their hormone, or for a small part only.

4. The *derotremous forms* and Siren, with their incomplete neoteny, do not retain the hormone in the thyroid. Here the cause of the neoteny is to be looked for in a dysfunction which induced a chronic deficiency of normal hormone, and a marked retardation and final arrest of the metamorphosis. The thyroids tried to supply the deficiency of hormone by an augmented production and increased in size.

5. The *perennibranchiate forms* with their complete neoteny abruptly retained their larval stage; this transformation was not an accommodation to their environment, and after the change the animals had to make the most of their condition as permanent inhabitants of the water. The development of the *derotremous forms* and Siren has been very gradual, because their ancestors gradually retained a more and more larval stage; so this transformation could take place under the influence of the claims of their surroundings, and could coincide with adaptations.

6. Nothing is known regarding the cause of the irregular function of the thyroids. It might be ascribed to want of iodin or changes in the circulation during the metamorphosis, or want of oxygen. There is no reason to assume that the cause was the same in all cases.

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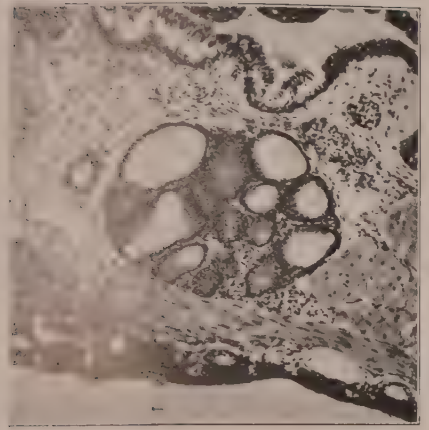
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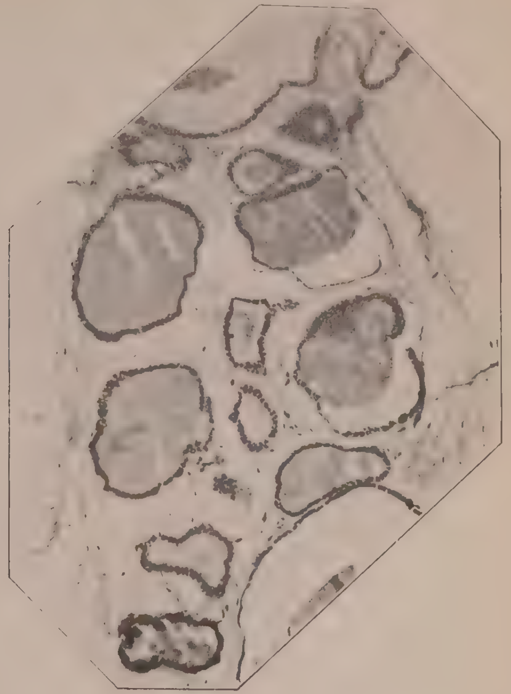
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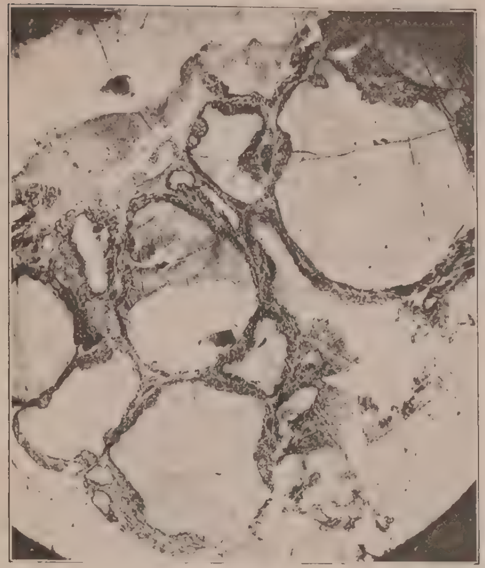
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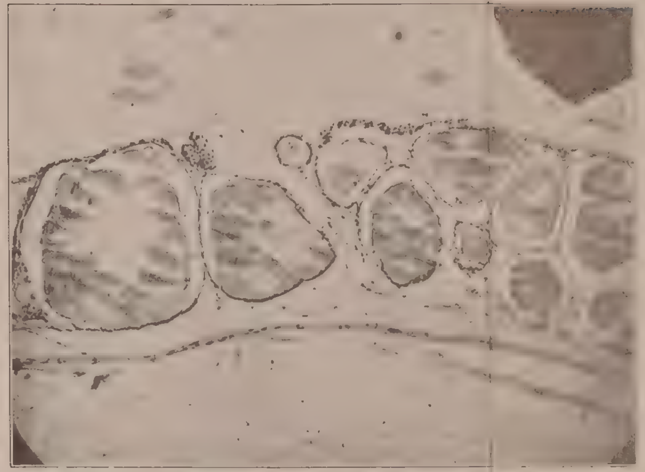
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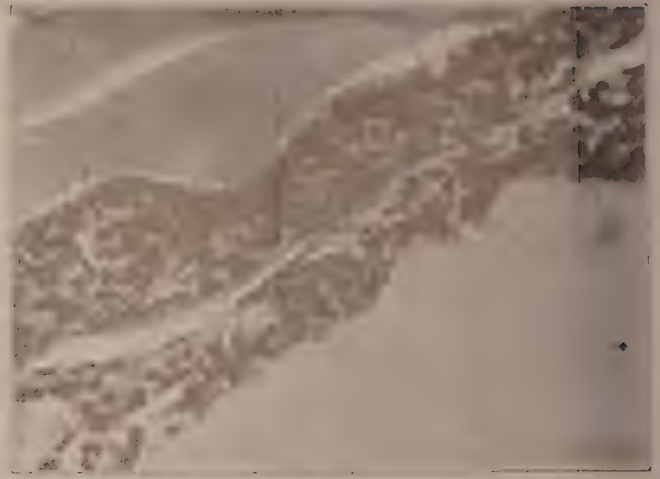
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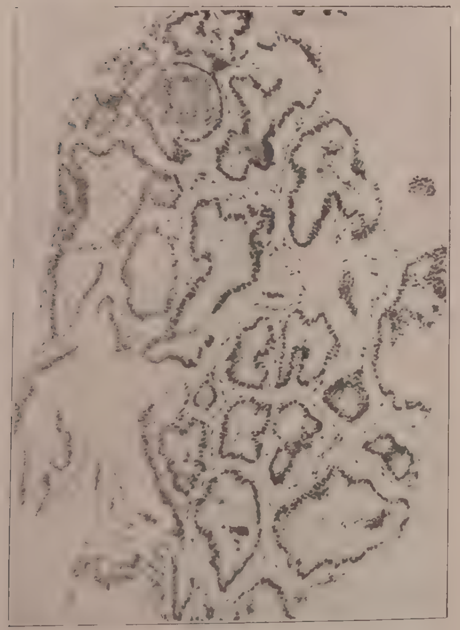
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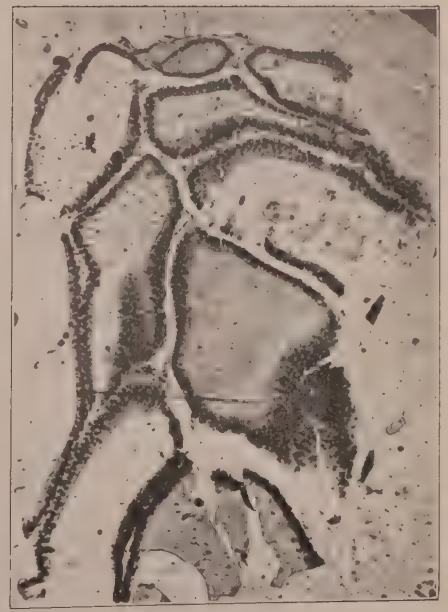
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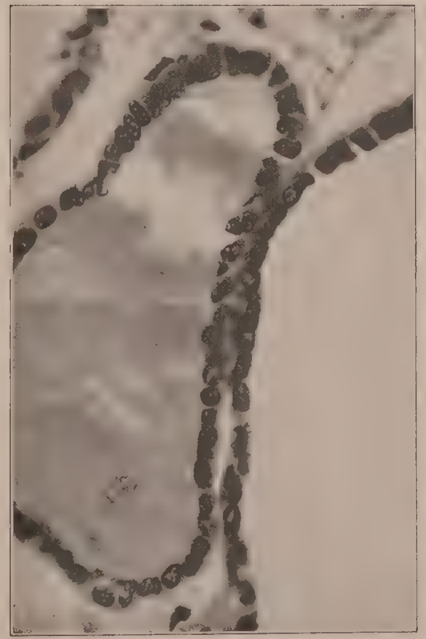
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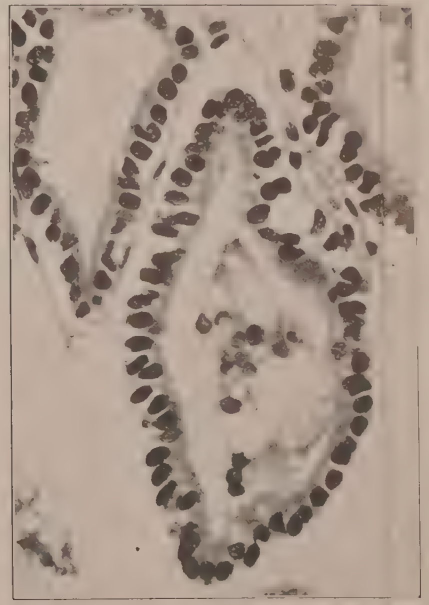
Fig. 8.

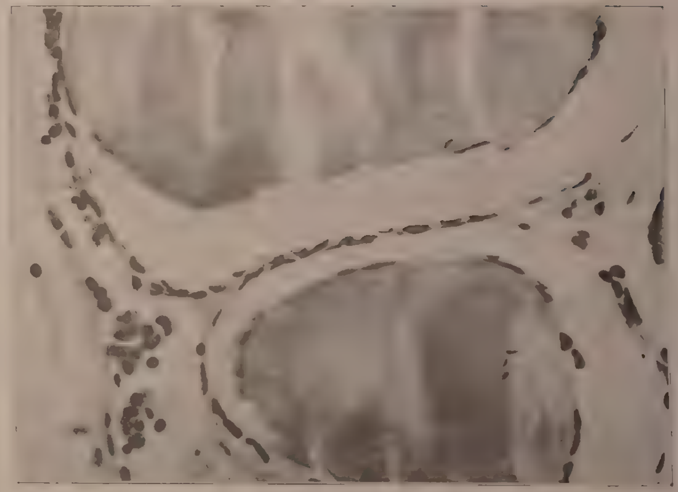
Fig. 10.

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EXPLANATION OF THE PLATE.

Fig. 1. Section through the thyroid of a normal adult *Salamander*, Onychodactylus japonicus; hematoxilin. × 40.

Fig. 2. The same of Necturus (spec. B); hematoxilin, eosin. × 40.

Fig. 3. The same of Amphiuma (spec. B); hematoxilin, eosin. × 40.

Fig. 4. The same of Amphiuma (spec. A); hematoxilin × 40.

Fig. 5. The same of Megalobatrachus maximus, of a specimen, examined by Mr. DE FREMERY. Body-length ± 110 cm. The thyroids were about 5 cm. in length, that is very large. Staining with hematoxilin and eosin. × 18.

Fig. 6. Section through the thyroid of Amblystoma mexicanum (ex. D), neotenous larva (axolotl). Staining with hematoxilin, eosin. × 40.

Fig. 7. The same of Necturus (spec. B); follicle epithelium greatly magnified; hematoxilin, eosin. × 190.

Fig. 8. The same of Amphiuma (spec. B); hematoxilin, eosin. × 190.

Fig. 9. The same of Megalobatrachus maximus (ex. DE FREMERY). Between the follicles very numerous bloodvessels filled with red blood corpuscles; hematoxilin, eosin. × 190. See fig. 5.

Fig. 10. The same of Amblystoma mexicanum (spec. D), Axolotl; hematoxilin, eosin. × 190.

Anatomy. — *"The relative weight of the braincortex in human races and in some animals and the asymmetry of the hemispheres."* By Dr. C. U. ARIËNS KAPPERS.

(Communicated at the meeting of September 26, 1925).

Although many investigations have been made on the weight of the cortex, at least in man, there are great controversies in the results. As the methods, by which the investigators have tried to solve this problem, always were indirect ones, this is not surprising.

So, using the figures, given by WAGNER [1]) and CALORI [2]) concerning the surface of the brain, DONALDSON [3]) (l.c. p. 202—204) calculated this weight by multiplying the surface with the average depth of the human cortex and its specific weight.

On account of his own measurements (l. c. p. 203) he estimated the average depth of the cortex, which, as we know, is locally varying in man (according to BRODMANN [4]) from 1,8 tot 4,0 m.M.) to be 2,9 m.M. With OBERSTEINER [5]) he took the S. W. of the human cortex to be 1,034.

DONALDSON, improving the researches of WAGNER by introducing a correction [6]) for the alcoholic shrinkage of the brainsurface so found the following figures:

Cases	Fresh T. B. W.[7])	T. W. hem.[8])	T. W. C. [9])	Proc. C. hem.
FUCHS	1499 gr.	1312 gr.	743 gr.	56.6 %
GAUSS	1492 „	1306 „	731 „	55.9 %
Workman KREBS	1273 „	1114 „	630 „	56.5 %
Woman 29 years	1185 „	1037 „	667 „	64.3 %
Average				58.3 %

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[1]) Massbestimmungen der Oberfläche des groszen Gehirns. Inaugur. Diss. Göttingen 1864.

[2]) Del cervello nei due tipi brachicefalo e dolicocefalo italiani. Memorie dell'Accademia delle Scienze dell'istituto di Bologna. Serie seconda, Tomo X. 1870 (p. 142—145).

[3]) The growth of the brain. A study of the nervous system in relation to education. London, Walter Scott ltm, 1895.

[4]) Ueber Rindenmessungen. Centralblatt f. Nervenh. und Psych. 1908 (p. 790) und Lokalisationslehre der Groszhirnrinde. Joh. Ambrosius Barth, Leipzig, 1909.

[5]) The average S.W. found by OBERSTEINER for the fresh cortex of man is properly 1.03305. Conf. OBERSTEINER. Anleitung beim Studium des Baues der nervösen Zentralorgane, 5te Auflage Wien, 1912, pag. 167 and Centr.bl. f. Nerv. h. k. 1894.

The average of the S.W. figures found by DANILEWSKY (already before OBERSTEINER) are also a little less. For the fresh human cortex this investigator found 1.0326. (Die Quantitativen Bestimmungen der grauen und weiszen Substanzen im Gehirn; Centralbl. f. d. mediz. Wissensch. N⁰. 14, 1880).

[6]) The figures found by WAGNER for the surface of both hemispheres together are: FUCHS 2210 cM², GAUSS 2195 cM², KREBS 1876 cM², and woman 2041 cM².

[7]) T. B. W. total brain weight to the calamus (without pia).

[8]) T. W. Hem. = total weight of both hemispheres.

[9]) T. W. C. = total weight of the cortex of both hemispheres.

The following table was composed by DONALDSON on account of the surface extension, found by CALORI in 22 brachycephalic and 19 dolichocephalic Italians, measured chiefly in the same way as WAGNER did (see below).

Number of cases	Aver. T. B. W.	Aver. T. W. hem.	Aver. T. W. C.	Aver. perc. C. per hem.
19 Brach. Ital. ♂	1336 gr.	1169 gr.	731 gr.	62.5 %
16 Dolich. „ ♂	1299 „	1135 „	690 „	60.7 %
3 Brach. „ ♀	1148 „	1005 „	635 „	63.2 %
3 Dolich. „ ♀	1110 „	971 „	595 „	61.2 %
Average				61.85 %

From this we see that, on account of the measurements of WAGNER, DONALDSON concludes at an average cortex weight percentage of **58.3**, on account of those of CALORI of **61.85** per hemisphere.

It is not without interest to point out, what is meant by weight of hemispheres in such cases. Two methods are used to sever the hemispheres from the remainder of the brain. We understand by hemispheres either all that lies before the corp. quadrigemina ant. or cut them off behind the corpora quadrigemina posteriora (immediately before the pons). The first way is used by BOYD (see below) and then the average weight of the hemispheres is about 87.5 % of that of the whole encephalon. The last method (mostly used) is followed by CLAPHAM, BROWNE and others (including myself).

The determination of the surface has been made by WAGNER and CALORI almost in the same manner.

The outer surface of the brain was covered by triangles and parallelograms of goldleaf or tinfoil. These again were spread out, measured and counted. The cortex in the depth of the sulci (which is almost $^2/_3$ of the whole surface) was determined by measuring the length and the average depth of the sulci and multiplying those figures with two. It is evident that this method contains a source of errors. Moreover the correction of the alcoholic shrinkage causes difficulties. Nevertheless such a correction is necessary, because the volume and the surface shrink considerably in alcohol.

This method, determining the cortical surface in alcohol material, was also applied by JENSEN [1] on brains of a paralytic, a melancholica and three idiots. He compared his results with those of WAGNER and found that the total cortex surface of his patients varied from 94 % to 75,3 % from the figures found by WAGNER for GAUSS, the lowest percentage being that of the brain of an idiot and the other percentages, although remaining below those of GAUSS and FUCHS, falling within the group of the woman and the workman examined by WAGNER (l. c. p. 752).

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[1] Untersuchungen über die Beziehungen zwisschen Groszhirn und Geistesstöhrungen an sechs Gehirnen geisteskranker Individuen. Arch. f. Psychiatrie 1875 Bnd. V, Heft 3.

His absolute figures are of no avail for my purpose, since he examined pathological material exclusively and his figures have been derived (as the original ones of WAGNER) from alcohol material.

His informations surely would have been of more value, if he himself had also measured the surface of some normal brains; comparisons of two authors being more reliable, since different authors rarely make the same mistakes. It is selfevident that with the relative smaller surface of these brains, also a smaller volume and weight of cortex has been calculated in such cases, as is made probable also by the researches of JÄGER and HENNEBERG on pathological material (l. c. infra).

While the method of all these authors was based on measuring the surface, the average depth and on multiplying these with the S.W. of the cortex, we see that besides the objections mentioned above, this method contains still another source of errors, viz. the question how to find the average cortical depth, which was estimated by DONALDSON to be 2,9, by JENSEN 2,98, and by DANILEWSKY and HENNEBERG 2,5 m.M.

JÄGER [1]) has avoided the use of an average depth figure, determining the volume of the cortex directly with the compensation planimeter (already used by ANTON [2])) in the following way:

JÄGER cut the brain, after it had been put for a short time in 5 % formaline, in slices of 1 c.M.

He then first measured the whole circumference of the brain (this being the external border of the cortex) with the planimeter and afterwards the circumference of the white substance (this being the internal limit of the cortex). The latter he substracted from the first and by this means determined the transverse surface of the cortex of each slice. This figure he multiplied with 1 c.M. thus calculating the volume of the cortex for each slice. For the poles he made corrections.

By multiplying the cortex volume thus found for the total brain with the S.W. 1,034, I determined the weight of the cortex. As, however, in his article the weight of the hemispheres is mentioned in one case only, the weightpercentage of the cortex of the hemispheres could be calculated in that case only. In a normal, four years old boy with a total brainweight of 1140 gr. and a weight of both hemispheres together = 997,5 gr. it amounted to 549 gr. or **55** % of the weight of the hemispheres (in an adult normal woman he found 557 gr. cortex).

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[1]) R. JÄGER. Planimetrische Messungen der Rinden- und Marksubstanz des Groszhirns. Inaugural Dissertation, Halle. 1910.

[2]) G. ANTON. Gehirnmessungen mittels des Kompensationsplanimeters. Wiener Klinische Rundschau: 1903. See also: Zur Kenntnisz der Störungen im Oberflächenwachstum des menschlichen Groszhirns, 1ste Mitteilung, Ibidem, Bnd. IX. 1888.

The planimetric method had been applied already in 1884 by CONTI, who, however, did not determine the whole mass of the cortex, but the relation between the white and the grey substance on three levels, the first *before* the basal ganglia, the second *through*, the third *behind* the basal ganglia, in 4 men and 2 women (Rapport entre la substance grise et blanche du cerveau humain: Internationale Monatschrift für Anatomie und Physiologie Bnd. 1, 1884).

Moreover Dr. ANITA TAFT has in 157 cases determined planimetrically the relation between the grey and white substance in the transverse level of the optic chiasm. She attained the interesting result that in children, microcephalics and mongoloid idiots the relation was in favour of the grey substance, in normal cases, manic depressives and praecox patients in favour of the white substance. See Journal of nervous and mental diseases. Vol. 47, 1918.

It appears that these figures of JÄGER are lower than those calculated by DONALDSON from the surface measurements of WAGNER and CALORI.

DONALDSON [1]) himself also tried to determine the weight of the cortex, in still another way, viz. by making use of the figures found by DE REGIBUS for the waterpercentage and the S.W. of grey and white substance. If a hemisphere (in casu cortex and white substance without striatum) is weighed and its volume known, we may calculate its average S.W. Knowing that the S.W. of the cortex is 1,034 and that of the white substance 1,041, we may calculate in a given case the relation between the amount of white and grey substance (in casu cortex).

From the figures of DE REGIBUS [2]), concerning the waterpercentage of grey and white substance (which closely coheres with its S.W.), DONALDSON calculated the quantity of cortex and came to a lower figure than calculated by him from the surface tables of WAGNER and CALORI.

He stated in his way an average of **54.8** % only, which is considerably lower than the **58.3**% derived from the surface measurements of WAGNER and the **61.85** % calculated from those of CALORI, and closely resembles JÄGER's (vide supra) result.

N⁰. of the brain	Weight 2 hem.	Weight cortex	Perc. cortex per hem.
N⁰. 1	1277 gr.	720 gr.	56.3 %
„ 2	1194 „	661 „	55.3 %
„ 3	1152 „	633 „	54.9 %
„ 4	1067 „	562 „	52.6 %
Average			**54.8** %

This makes us suppose that the figures found by WAGNER and CALORI for the surface are too high, a supposition that is confirmed by HENNEBERG's [3]) work, who determined the surface of the brain in a more exact way. I shall mention HENNEBERG's method below, but already will mention at once that, whereas DONALDSON (l.c. p. 205) on account of WAGNER's figures finds a surface of 2352 cM^2 in a brain of 1360 gr. T. B. W. and CALORI in a brain of 1325 gr. a surface of 2439 cM^2., HENNEBERG only finds a surface of 2052 cM^2 in a brain of similar weight (1320 gr.), consequently 15 % less [1].

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[1]) l.c. p. 204.

[2]) Published in Giacomini: Guida allo studio delle circonvoluzioni cerebrali dell'uomo Torino, 1884.

[3]) HENNEBERG. Messung der Oberflächenausdehnung der Grosshirnrinde. Journal für Psychologie und Neurologie, Bnd. 17, 1910—11.

Probably the surface measures of HENNEBERG are more exact than those of WAGNER and CALORI. Whereas these authors divided the brain only in hemispheres or lobes, determining the surface hidden in the sulci only indirectly, HENNEBERG measured this hidden surface also directly, by cutting the cortex (after fixation of the brain in 10 % formaline) in pieces of 1 to 3 cM^3. In this way all the cortexsurfaces could be reached easily and measured directly.

For this purpose he used pieces of silkpaper, which does not swell in water, and then he measured all the pieces together by lifting them under water from the cortex and putting them on milligraphpaper. As objects he used (one case excepted) only the left hemispheres.

In this way he examined three Hannoverians, one Hottentot, one Herero and one Javanese. The cortexweight is calculated by taking the S.W. = 1.034 and the average depth with HENNEBERG [2] and DANILEWSKY (l.c.) = 2.5.

Cases	T. B. W.	Average left hem.	Surfage left hem.	Cortex left hem.	% Cortex hem.
German I ♂ 45 j.	—[3]	525 gr.	1082 cM^2	279.5	53.4 %
„ II ♂ 22 j.	1510 gr.	655 „	1240 „	320.5	48.9 %
„ III ♀ 26 j.	1320 „	565 „	1016 „	262.6	46.5 %
Average					**49.6 %**
Hottentot ♂	—[3]	615 „	1119 „	289.0	47.0 %
Herero ♂	1215 „	530 „	996 „	257.5	48.6 %
Javanese ♀	1230 „	535 „	1050 „	271.5	50.7 %

Hence results that HENNEBERG found a still lower average percentage for Europeans (**49.6 %**) than DONALDSON calculated from the S. W., but also that in his Germans he found variations from 46,5 % to 53,4 %.

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[1] TRAMER who determined the surface of the right hemisphere of a normal woman of 35 years came to a figure still 20 % lower than HENNEBERG found for a woman of 26 years. As, however, TRAMER does not mention the T. B. W. of his woman, this figure is uncontrolable. It seems too small even for an average female T. B. W. of 1250 gr. (HENNEBERG's woman had a high brainweight though, this being 1320 gr. which however seems to occur more in Hannover: KRAUSE). See TRAMER: Messung und Entwicklung der Rindenoberfläche des menschlichen Groszhirns. Arbeiten aus dem neurologischen Institute Zürich, Bnd X, 1916.

[2] HENNEBERG himself made his calculations estimating the S. W. = 1,03; I made them using a S. W. = 1.034, this being more exact. The average difference is 0,3 % per hemisphere and 0.12 % per T. B. W.

[3] In this case the total brainweight is not mentioned by HENNEBERG.

While all these methods of determining the cortexweight are indirect ones and so, probably are more open for errors than a direct method, I made *direct weighings* of the cortex in the following way:

Brains, hardened in formaline[1], were weighed and afterwards halved in the sagittal diameter. Then the cerebellum and the pons were cut off along the corpora quadrigemina posteriora and the hemispheres were weighed. Afterwards these hemispheres were cut by the macrotome of REICHERT, in slices of 2 to 3 m.m. During 3—6 hours these slices were coloured in an aqueous nigrosine solution (1 : 1000), upon which the grey substance marked out almost black against the almost uncoloured white substance.

These slices I put on glass plates and severed the cortex by means of a thin knife. Then I weighed the cortex, after all the pieces (cortex and rest of hemisphere) had evaporated so much that the cortex plus the rest represented again the same weight the hemisphere had before being coloured in the nigrosine solution. This drying is necessary, as by their large surface the pieces absorb a large quantity of water.

In total 6 brains (12 hemispheres) were treated in this way: three Dutch and three Chinese brains from the Dutch East-Indies (formaline material).

My results are expressed not only in percentages of the hemisphere weight, but also in percentages of the T. B. W., the latter giving a more reliable figure for comparison of the left cortex and the right one.

LEFT HEMISPHERES

Cases	T. B. W.	Weight l. hem.	Weight l. cortex	Weight l. rest	% cortex p. hem.	% cortex p. T.B.W.
Dutch. X. ♂ 29 y.	1068 gr.	—474.5 gr.	237 gr.	237.5 gr.	49.99 %	22.2 %
„ Gr. ♂ 42 y.	1375 „	+618 „	+299 „	319 „	48.38 %	+21.74 %
„ Bo. ♂ 18 y.	1360½ „	—621 „	331 „	290 „	53.3 %	24.32 %
Average l.					**50.8 %**	
Chinese I. N⁰. 11	1014.5 „	—430 „	+218 „	212 „	50.0 %	+21.49 %
„ I. N⁰. 10	1344 „	—576 „	+300 „	276 „	52.1 %	+22.32 %
„ I. N⁰. 12	1425.5 „	—615.5 „	313.5 „	302 „	50.9 %	22.0 %
Average l.					**51.0 %**	

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[1] That as well the weight as the volume increase a little (± 1 % FLATAU) in formaline, does alter the *relation* between cortexweight and hemisphereweight only in a very small proportion. The same avails for the aqueous 1 % nigrosinesolution. The influence, exercised by the formaline-fixation, in my opinion is even smaller than the greater or smaller quantity of blood in the brain, as the S. W. of the blood is considerable and the vascularisation of grey and white substance differs much.

RIGHT HEMISPHERES

Cases	T. B. W.	Weight r. hem.	Weight r. cortex	Weight r. rest	% cortex p. hem.	% cortex p. T.B.W.
Dutch X. ♂ 29 y.	1068 gr.	+477.5 gr.	+238.5 gr.	239 gr.	49.94 %	+22.33 %
,, Gr. ♂ 42 y.	1375 ,,	—613 ,,	297 ,,	316 ,,	48.4 %	21.16 %
,, Bo. ♂ 18 y.	1360½ ,,	+622 ,,	+336 ,,	286 ,,	54.0 %	+24.6 %
Average r.					**50.6 %**	
Chinese I. N⁰. 11	1014.5 ,,	+437.5 ,,	212.5 ,,	225 ,,	48.61 %	20.94 %
,, I. N⁰. 10	1344 ,,	+584 ,,	297 ,,	287 ,,	50.86 %	22.1 %
,, I. N⁰. 12	1425.5 ,,	+638 ,,	+320 ,,	318 ,,	50.11 %	+22.45 %
Average r.					**49.9 %**	
Average for all hemispheres of the Dutch					**50.65 %**	
,, ,, ,, ,, ,, ,, Chinese					**50.45 %**	

The halving of the brain being never exact the cortexpercentage per hemisphere is influenced by the inexact halving of the brain, whereas we use the same constant, in expressing the cortexpercentage (right and left) in the total brain weight.

Doing so I found the average cortexpercentage per hemisphere to be **50.65 %** in the Dutch, this being almost 1 % more than the figures, found by HENNEBERG in his Hannoverians. This amount (1 %) however falls within the individual variations in the West European races, showing an upperlimit of 54,0 %.

The percentage in the Chinese, mentioned above differs only 0,2 % from the Dutch, which is very little, and falls within the errors inevitable in such examinations. This result is in striking contrast to CLAPHAM's [1]), who, estimating the depth of the braincortex in Chinese coolies of Hongkong (and of Pelewislanders) concluded: "although destitute of any means of accurately measuring the depth of the grey matter of the cerebral convolutions I am convinced that it was appreciably shallower than in the same structure in the average European".

As to an eventual difference between the left and right cortex, my results show that once the right, another time the left cortex was, or seemed to be a little heavier. I value this difference the less, because it depends mostly on absorbed water. If we allow the pieces of cortex half a day to evaporate, the difference between right and left becomes a minimal.

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[1]) CROCHLEY CLAPHAM. On the brain weights of some Chinese and Pelewislanders. Journal of the Anthropological Society of Great Britain and Ireland. Vol. VII 1878, pag. 92.

Much has been written on an eventual asymmetry.

BROCA [1]) found in the average the *right* hemisphere of men 1,93 gr. heavier than the left, in women the same hemisphere 0,03 gr. heavier; BOYD [2]), however, says: "it is a singular fact confirmed by the examination of nearly 200 cases at St. Marylebone in which the hemispheres were weighed separately that almost invariably the weight of the *left* hemisphere exceeded the weight of the right one by at least the eighth of an ounce", (a very small difference indeed, the eight of an ounce being 3,7 gr. so the difference in an average brain weight of 1360 gramme would be only 0,27 $^0/_0$; DONALDSON).

Dr. THURNAM (quoted by BROWNE) in the contrary again found the *right* one heavier. According to CRICHTON BROWNE [3]) it is a question of age. In 400 lunatics he found the right hemisphere predominating with the exception of women between 40 and 60 and men between 50 and 60, in as much as here the left hemisphere would be a little heavier. He found the greatest differences to exist under 20 years and then always in favour of the right hemisphere, this also being the case with people older than 70 years.

In contrary to the results above mentioned FRANCESCHI [4]) found in 157 male brains in 49 cases the left hemisphere and in 51 the right one heavier, while in 57 cases they practically were of equal weight.

In 144 female brains he found in 43 cases the left hemisphere, in 46 cases the right one heavier and in 55 cases both hemispheres of equal weight (or varying in decimals of grammes). Also WAGNER (l.c.) and BRAUNE [5]) sometimes found the left, sometimes the right hemisphere a little heavier.

DONALDSON supposes that, if the brain is always halved in the same position e. g. on the base, the occipital pole directed to the cutter, a righthanded anatomist will allways make the same error.

This personal error, in halving the brain, vanishes in weighing only the cortex, as the cortex of both hemispheres nowhere meets, the cortex of each hemisphere being isolated. So the comparison of the quantity of cortex in the right hemisphere and the left one gives a more trustworthy criterium for an eventual asymmetry, especially if we express both in the same constant, viz. in $^0/_0$ of T.B.W. The figures found by myself also prove that none of the hemispheres is constantly superior in cortexpercentage. [1]).

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[1]) Cited by TOPINARD in his Eléments d'Anthropologie générale p. 582—583. Paris 1885.

[2]) BOYD. Tables of weight of the human body and its internal organs etc. Philosophical Transactions of the Royal Society of London. Vol. 151, 1861.

[3]) CRICHTON BROWNE. The weight of the brain and its component parts in the insane. Brain Vol. I 1879 p. 516.

[4]) Bollettino della Societa di Scienze mediche di Bologna 1888. Quoted after DONALDSON.

[5]) BRAUNE. Das Gewichtsverhältnisz der rechten und linken Hirnhälfte beim Menschen. Arch. f. Anat. und Physiol. 1891.

In three cases (marked in my table by †) the right cortex was a little heavier, in three other cases (marked also by †) the left. HENNEBERG, though examining chiefly left hemispheres, has in one case (his European No. III with a T. B. W. = 1320 gr.) compared the surfaces of both hemispheres and found on the right 1035 $c.M^2$., on the left 1026 $c.M^2$, the result (multiplied with 2,5 as average depth and 1,034 as S. W.) being only a difference of fully five grammes (0,3 % per T. B. W.) in favour of the right cortex. This figure is within the radius of errors, as is also the average surplus of the right cortex in some of my brains (4,3 gr.) and of the left one in others (3,5 gr.).

My results show at best that the left cortex and the right one never are exactly equal in weight and that once the left and an other time the right one is or seems a little heavier. Nor in animals did I find a constant preponderance (see next page). This accords with the results of FRANCESCHI, WAGNER and BRAUNE, who too, in the hemispheres, found sometimes the left, sometimes the right one a little heavier.

Moreover my results show that halving the brain is a very poor way indeed, to determine any *superiority* of one hemisphere. Whereas of my six brains in one case only, the left hemisphere was heavier, in the other five cases the right one, the cortex determinations show that in three cases the left cortex percentage per T.B.W. was heavier, in the other three the right one. So in two cases (Chinese 11 and 10) in which the left hemisphere seemed to be lighter the cortex was nevertheless heavier.

Here already I should like to remark, that the calculation of cortexpercentage per T. B. W. is of value only for the mutual comparison of the right cortex and left one of one and the same cerebrum, not for the cortexpercentages of different individuals, as in another paper (see the following issue of these proceedings) I shall prove, that the weight of the cerebellum (being an important factor also in the T.B.W.) shows very large personal variations, as well in the Dutch as in the Chinese (from 8 to 12 % of the T. B. W.).

To conclude some remarks on the cortexweight in animals.

Nor here direct weighings have ever been made.

WAGNER measured the surface of the cortex in an Orang, and found it to be 533.5 $c.M^2$, and HENNEBERG found in an Ateles (with a T.B.W. = 142,5 gr. and a hemisphere weight = 64.5 gr.) a surface of 172 $c.M.^2$ As, however, neither the average depth, nor the S.W. of the cortex is known in these animals, we cannot conclude from these figures to a weight percentage.

Supposing the S. W. in WAGNER's case also to be 1,034, and the average depth = 2,47 m.M [2]), the Orang of WAGNER would have a cortexweight almost equal to the cortexweight of my Orang.

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[1]) This does not eo ipso exclude (areal) local weight asymmetries, although I doubt their constancy. See however also MELLUS. Anat. Record. V. 1911.

[2]) According to MARBURG the average depth of the cortex, calculated from the frontal, central, temporal and occipital lobus, is even a little bit larger (2,53 m.m) l.c. p. 585.

I weighed the cortex of a Marsupial (Macropus robustus), an Edentate (Choloepus didactylus), an Ungulate (horse), a Carnivore (dog), two katarrhine apes (Semnopithecus cephalopterus and Hylobates syndactylus) and an Anthropoid (Orang). The figures found for these animals, are shown in the following table.

Examining these figures more closely we observe that, in each of these animals the average cortexpercentage of both hemispheres is as large, or in most cases (Choloepus, Dog, Hylobates and Orang) even larger than in Man, this being a consequence of the fact (see below) that smaller brains generally have more grey matter than white matter. So we also understand the observation of Miss TAFT, who found in children, microcephalics (and mongoloid idiots) a cortexpercentage, arger than in normals (l.c.).

Next to this statement two more facts are striking in this table.

LEFT HEMISPHERES

Animals	T. B. W.	Weight l. hem.	Weight l. cortex	Weight l. rest	% cortex per hem.	% cortex p. T. B.W.
Macropus rob.	55 gr.	20.5 gr.	10 gr.	10.5 gr.	48.7 %	18.2 %
Choloepus did.	34 „	13.1 „	7.1 „	6 „	53.8 %	+20.88 %
Canis fam.	78.5 „	34.1 „	21.1 „	13 „	61.9 %	+26.95 %
Equus cab.	510 „	187.2 .	96„2 „	91 „	51.3 %	+18.86 %
Semnopith. ceph.	65 „	27.6 .	13„1 „	14.5 „	47.3 %	20.15 %
Hylobates syn.	105 „	43.0 „	25 „	18„0 „	58.14 %	23.8 %
Simia satyrus	293 „	122.7 „	67„2 „	55„5 „	54.77 %	22.87 %

RIGHT HEMISPHERES

Animals	T. B. W.	Weight r. hem.	Weight r. cortex	Weight r. rest	% cortex p. hem.	% cortex p. T. B.W.
Macropus rob.	55 gr.	20.5 gr.	10 gr.	10.5 gr.	48.7 %	18.2 %
Choloepus did.	34 „	13 „	7 „	6 „	53.8 %	20.58 %
Canis fam.	78.5 „	33 „	20.5 „	10.5 „	62.1 %	26.18 %
Canis f. collie	77.7 „	32.35 „	20.0 „	12.35 „	61.9 %	25.74 %
Equus cab.	510 „	185 „	96 „	89 „	51.9 %	18.82 %
Semnopith. ceph.	65 „	26.5 „	13.5 „	13 „	51.0 %	+20.77 %
Hylobates syn.	105 „	44 „	25.5 „	18.5 „	58 %	+24.3 %
Simia satyrus	293 „	122.5 „	69.5 „	53.0 „	56.73 %	+23.64 %

Firstly the high cortexweight per T. B. W. in Canis is astonishing[1]), especially in comparison with Semnopithecus, which has a smaller brainweight and a higher standing in the phylogenetic series. With both these facts we should rather expect a larger cortexpercentage in Semnopithecus, the larger development of the brain in apes causing the pallium to be developed more than the stem.

That a heavier cerebrum ought to have less cortex relatively than a lighter one (at least in the same group or in related animals) is explained by ERNST DE VRIES[2]) and HOVY[3]) who showed that, if the brainvolume increases (in related groups), the white matter must increase relatively more than the grey one[4]).

Now dogs and apes are not related but still both are gyrencephalic animals and by the lower standing of the dog as well as by his larger brainvolume we would expect Canis to have a lower cortexpercentage than Semnopithecus.

This not being the case, but in the contrary Canis having a surprisingly high cortexpercentage, consequently that can be explained only by the large development of the mantle and the depth of the sulci in this animal.

It would not surprise me, if the relation between the superficial cortex and the hidden cortex (being in man in the average 1 : 2 and in Orang 1 : 1,56) would be larger in Canis.

That the mantle of the brain is exceedingly developed in the first dog, also results from the fact that his hemispheres amount to 86,8 % of the T. B. W. (in the collie 83,3 %), in my apes the average being 82,9 % only.

A second remarkable fact is the high cortexpercentage in *Hylobates*. Although the cortex percentage in the Orang as well as in Hylobates is high, in the latter it is still higher than in the former.

We cannot be surprised that in the Orang the cortexpercentage per T.B.W. is higher than in Semnopithecus, since in anthropoids the mantle of the cerebrum is more developed than in Semnopithecus.

That however Hylobates has a higher cortexpercentage than the Orang cannot be explained by its smaller brainvolume alone, since from this standpoint the cortexpercentage in the still smaller brain of Semnopithecus ought to be still higher than in Hylobates. Which is not so.

That Hylobates has a greater percentage than *both* other apes can be only explained by a larger depth of the cortex in Hylobates than in the other apes mentioned above.

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[1]) A second examination of the right hemisphere of a collie confirmed this fact, which besides is also in harmony with the results of DANILEWSKY (l. c.).

[2]) ERNST DE VRIES. Das Corpus striatum der Säugetiere. Anat. Anzeiger Bnd. 37, 1910.

[3]) HOVY. On the relation between the quantity of white and grey substance in the central nervous system. These Proceedings 16, p. 311, 1913

[4]) The lower cortexpercentage in Equus falls within this group.

This explanation agrees with the measurements of Marburg [1]). This author also emphasizes „dasz die Rindenbreite des Hylobates absolut gröszer ist als die des Orangs, letzere aber gröszer als die der anderen untersuchten Affen." (l. c. p. 596).

This is in perfect harmony with my results.

At last still one remark.

Comparing my results with those of DONALDSON [2]) for the Norwegian rat, we find (l. c. p. 87) the cortexvolume (XX): being 393,15 m.m., the spec. weight = 1,05 (l.c. p. 76), the cortexweight to be 0,4128 gr. in the rat. The brainweight in this group being 2,054 gr. (l.c. p. 87), the relation of the T. W. C. to the total brainweight = 20,1 $^0/_0$ or in one hemisphere 10,05 $^0/_0$ per T. W. B.

This is a much smaller percentage than in my animals and in man. We know, however, that in most gyrencephalic animals more cortex is found in the sulci than on the surface, and ought to consider that the rat is lissencephalic. Were apes and man also lissencephalic, i.e. were there no cortex hidden in the sulci, the cortexpercentage of a hemisphere per T. W. B. would be even less than in the rat and amount to 7 $^0/_0$ scarcely, whereas it actually is in man and the higher apes more than 22 $^0/_0$ per T.B.W.

So also by my figures we may realize the great importance and necessity of fissuration for higher cortical development.

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[1]) MARBURG. Beiträge zur Kenntnisz der Groszhirnrinde der Affen. Arbeiten aus dem Neurolog. Institut in Wien, 1907.

[2]) DONALDSON. The rat. 2d. ed. Memoirs Wistar Instit. Philadelphia 1924.